THESIS FOR THE DEGREE OF Ph.D.

THE FUNCTION OF COKE IN THE BLAST FURNACE.

by

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INTRODUCTION.

An analysis of the industrial development of coke manufacture with its present bias towards output productivity, and the problem of the future evolution of the industry in the control of coke quality.

If current scientific literature is indicative of future industrial evolution, then the trend of these developments in the manufacture of coke will lie in the gradual supersession of the present empirical methods of production by scientific reproduction of coke qualities to specification. In publications concerned with coke research this probable conversion in industrial practice finds its expression in the attempted particularisation of considered fundamental coke qualities, not merely by theoretical definition but supported by quantitative measurement of such qualities in themselves and of their behaviourism. In the author's opinion this is not a fortuitous development, but a logical reaction characteristic of present industrial practice against the pronounced absorption of industrialists in introducing modifications and extensions of plant, which increase productive output without effecting a corresponding improvement in the quality of the marketed product for its intended use (1,2). The modicum of scientific control, where exercised in modern coking practice, is but the laboured experience of repeated trial-and-error tests, by which either partial or temporary adjustments have been made to the newer conditions operating in the coke consuming industries. If it be conceded, however, that the future of the coke industry lies in the quality rather than in the quantity of coke produced, then the increasing pressure of scientific advances in these associated industries will inevitably have to be parallelled by a similar intensive attack on coke problems, incapable of solution by the previous laggard and unsatisfactory methods of research. The inherent difficulties associated with the controlled reproduction or elimination of qualities, desirable or otherwise in coke, are only too apparent and the further complications afforded by the incidence of local peculiarities of the coal

base equally discouraging. Nevertheless, such circumstances should not act, as in the past, as a complete deterrent to the initiation of a systematic investigation, which, with a complementary effort on the part of coke users, will assure the suitability and efficient performance of a coke, under the specified conditions of its proposed use.

The failure to establish a proper balance between production and quality is not to be attributed entirely to the shortcomings of research workers, since the stages of industrial growth of coke processing are the resultant of the interplay of economic, social and geographical forces at the level of scientific knowledge of the period. This introduction is confined to the influence of research in the development of the industry, while recognising the role played by other factors. Originally, the coking industry was initiated by the discovery of the astonishing variety of products to be obtained by the destructive distillation of coal. The market for such products extended over the whole range of industrial activity. Dyes, explosives, oils, fertilisers, disinfectants were all to be obtained by a simple thermal treatment of a raw material, indigenous to the country and available in almost unlimited quantity, and to the organic chemist was given the problem of classifying and augmenting, improving and extending the uses of this large variety of carbon compounds. So long as the value of coke was economically and industrially of secondary importance compared with the volatile by-products of the distillation, the problem of coke research was not considered as of any great moment. The essentially analytical outlook of the chemist naturally devised methods for ascertaining the chemical purity of the cokes, and these quantitative determinations served, within the limits agreed on by producer and consumer, as a restriction on the ash, moisture, sulphur and, in special cases, phosphorus content of the cokes. The advance since these early days can be gauged by recognising that today chemical

standardisation of the products from the ovens is the only purposeful control of quality finding practical application, and is exemplified in industrial practice by the washing and blending of the coal charges, although other advantages are to be gained from such pre-treatments.

With the imposition of economic forces from outwith the industry itself (mentioned below), the status of coke on the production sheet was raised and compelled a greater measure of scientific control and improvement of its basis properties to be taken. The problem was not simply one of increasing output to meet increasing demand, which could be, and was, successfully tackled by the co-operative effort of the refractories expert, the chemical engineer and the metallurgist. What was required was a specialised knowledge for research on surface chemistry, e.g., X-ray technique, which is only now becoming available with sufficient precision for scientific work on coke. The purely chemical test had obvious limitations in the study of coke activities, since chemical equivalence between cokes was no criterion of identity of physical characteristics. The exact significance of the one other laboratory chemical test, the wet oxidation test, has still to be determined and its results correlated with the behaviour of coke in practice. Alternative procedures for the study of solid surfaces were rendered useless by those inherent difficulties of coke surfaces, quoted previously; its heterogeneity, petrographically and chemically, its insolubility in chemical reagents, which precluded staining or etching and the problem of preparing polished surfaces of representative samples. The obvious method of eliminating these handicaps was by the proper use of statistical methods, i.e., the use of bulk samples in a small scale test, which could be made to simulate the conditions of its later industrial experience. Such tests as the shatter test, the producer test, the Midland Combustibility test, are examples of this type of technique, which contributed in whole or in part to the adoption

of the empirical concept of coke testing (3). It is doubtful if such an approach to solve the pressing need of a measure of scientific control in coke manufacture will lead to eventual success, and as an example of the complexity of the problem consider the following two extreme conditions of the use of coke.

The blast furnace technician with his modern methods of intensive working, greater burdens, poorer ores, etc., is demanding improved qualities of coke. At the other extreme, the householder with his awakening social awareness of the benefits to be gained from a purer atmosphere, but unwilling to abandon the psychological warmth to be obtained from a "coal" fire, is creating a demand for a solid smokeless fuel. Since it is unlikely that the same type of coke will satisfy both consumers, it behoves the manufacturer to create the appropriate cokes. Yet, even were he willing to set aside part of his plant for the production of cokes with different properties, he would be handicapped by an ignorance of the desirable qualities of the fuel for the conditions of its proposed use; or, if these qualities were known, the problem of their quantitative reproduction in industry would still remain. Responsibility for the present lax state of affairs (and for its solution) is not solely that of the coke makers, but must be apportioned between the industrial consumers and the makers of combustion appliances. The latter, recognising the position, are discharging their responsibility through the work of their own research institution and, to their credit, lies the adoption of the well fireplace as an alternative to the inefficient grate, and the marketing of controlled automatic stokers for boiler equipment. As for the iron producer, the introduction of a scientific preparation of coke must follow on a solution of the mechanism of ore reduction and the removal of other obscurities surrounding blast furnace reactions. The role of coke in the blast furnace is by no means certain, and this uncertainty is reflected in the

results of the many field tests which have been made to ascertain this function. There is no lack of evidence that the problem has been recognised by responsible circles, who have initiated some movement to remedy the present situation. The British Iron and Steel Federation, for example, partially support three Coke Committees, who are charged with conducting a "programme of research on a national basis, which.....has full regard for those fundamental aspects that require consideration"(4). This national aspect has been stressed by complete Government maintenance of the Fuel Research Board, and the co-operation of the Blast Furnace Owners of the country and other interested consumers, practically and financially in these institutions, testifies to their ramifying importance. Such organisations are significant of a real desire to end the present trial-and-error deadlock and, in its place, develop certain guiding theoretical principles based on the co-ordinated research of the interested industries.

In 1937 the Scottish Coke Research Committee determined on a long term programme of research to study the function of coke in the blast furnace and, as a first stage, the property of combustibility (as defined in Chapter 2) was chosen as an essential quality to be measured within the terms of its definition by some laboratory test, and correlated with blast furnace practice in respect of the desirable values of combustibility. The results of these investigations are the subject matter of this thesis.

The experimental work of Chapter 1 is designed to determine the physico-chemical changes in coke on heating in vacuo, and the superficial reactions with oxygen and nitrogen. This chapter is complete in itself, since its results could not be logically developed to create further possible methods of solution of the problem of combustibility.

Chapter 2 introduces a particularly adaptable technique for measuring the velocity of a solid/gas reaction which, if adopted

as part of the routine testing of coke in industry, could be used in an interpretation of the working anomalies of the blast furnace. It affords a simple quantitative method of distinguishing the combustible properties of industrial cokes within wide and practical limits of combustion conditions, and it confirms the existence of a mathematical relationship of the variables of combustion based on a generally assumed theory of the process of combustion.

The manifest deficiencies of industrial cokes as standards for the accurate determination of general laws relating the variables of solid fuels lead to the laboratory production of uniform coke test pieces under known and reproducible conditions. Chapter 3 is virtually an essay on the experimental permutation of carbonising variables and the singular effect of each of these variables on combustibility, as measured by the test of Chapter 2. The importance of the particle size of the coal and the rate of heating of the charge are demonstrated, and a theoretical co-ordination of the results of these tests ventured to include all aspects of coke production.

CHAPTER ONE.

The physico-chemical changes in cokes on heating to 1400°C in vacuo, and the superficial effects of oxygen and nitrogen atmospheres at this temperature.

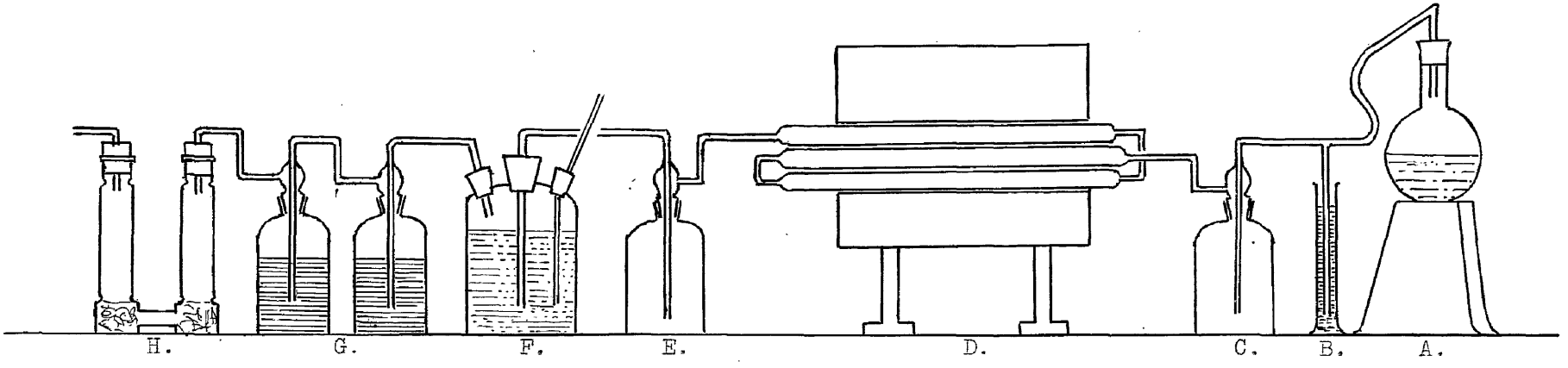
The experimental work detailed in this chapter had as its conscious guiding feature an attempted estimation of the activity of any coke surface when allowed to proceed to near-equilibrium under various atmospheric conditions. Such experiments were expected to translate into quantitative measurement the conception that the reactivity of coke was a continuously repeated reaction, tending to equilibrium, affected primarily at the boundary of the solid/gas system. The probable nature of this reaction is indicated, and its dependence upon the surface condition of the solid, in itself a variable with temperature, has also led to an investigation of the physico-chemical stability of coke at high temperatures.

The apparatus designed for such high temperature work has been developed in the conduct of the metallurgical research of the Royal Technical College (5), but for the particular conditions of the present research certain modifications and improvements of the original design have been introduced. For convenience, the description of the apparatus will be considered in three separate sections; (a) the cracking train, (b) the furnace proper, and (c) the measuring instruments.

The oxidation of molybdenum in air at temperatures above 500°C and the volatilisation of this oxide at higher temperatures form a chemical cycle, which in the case of an exposed electrical winding of this metal would result in a continuous reduction in the cross-sectional area of the wire, and latterly in failure. The use of such a heating element, therefore, necessitated a suitable atmosphere for the preservation of the molybdenum winding of the furnace proper. This "neutralising" atmosphere was the mixed product of the dissociation of ammonia vapour (nitrogen and hydrogen), and was obtained by the several stages of the cracking train shown diagrammatically in Fig.1.

Fig. 1.

Train for the Provision of "Neutral" Atmosphere to Molybdenum Furnace.

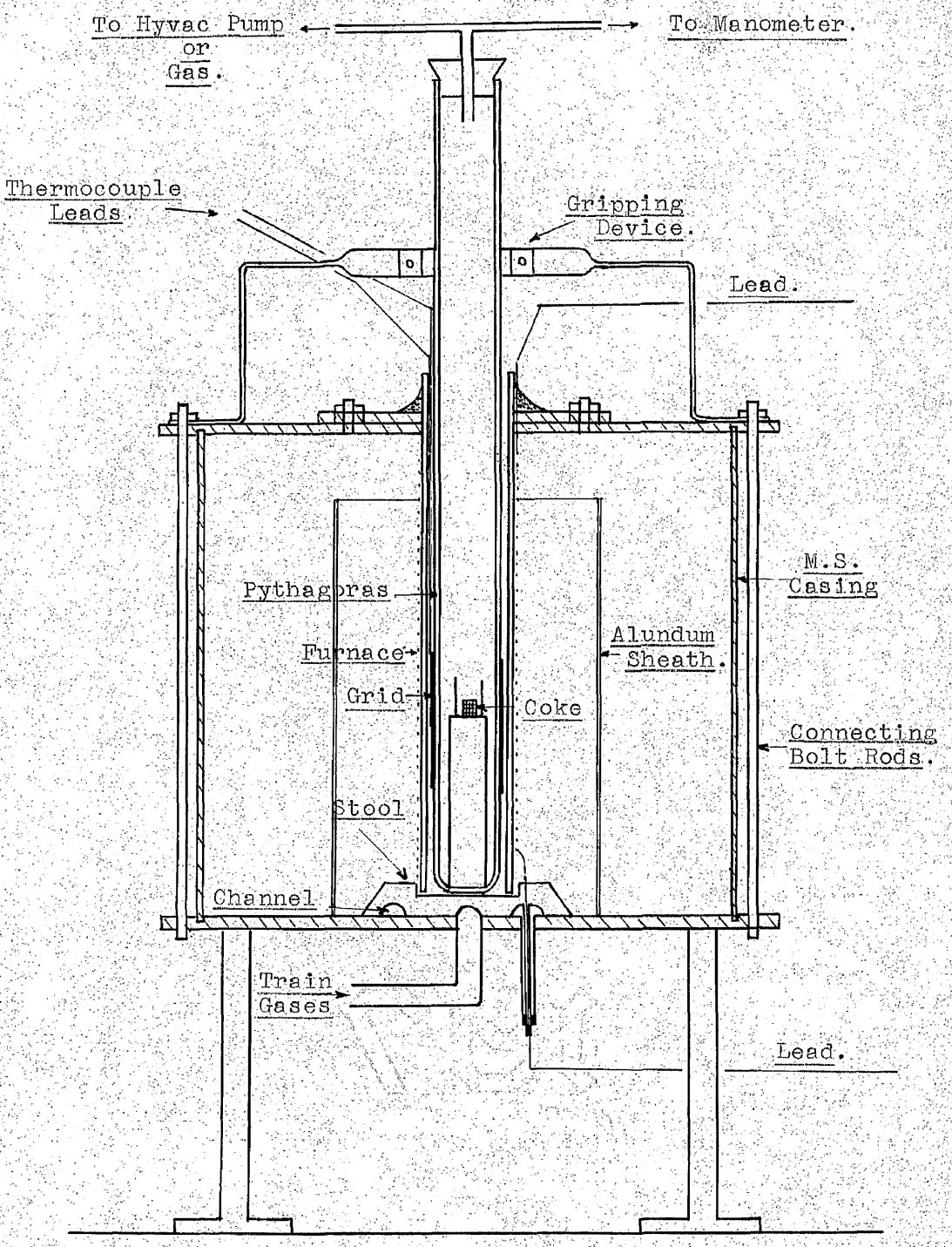


A = Flask of Ammonia.
B = Mercury Safety Valve.
C = Trap.
D = Morganite Tubes.
E = Trap.
F = Washer.
G = Sulphuric Acid Bottles.
H = Calcium Chloride Towers.

Sufficient concentrated ammonia (sp.gr. 0.88) was added to flask A to provide a steady current of mixed gases for 10 hours. The ammonia vapour from A, controlled by the rate of heating, passed to the empty wash bottle C, a trap to prevent any liquid being sucked into the furnace D. B, a measuring cylinder holding 6 inches of mercury, acted as a safety valve and outlet for the release of any dangerous excess pressure developed by the ammonia. From C, the vapour passed through three Morganite combustion tubes (36" x 1" I.D) - these connected in series by glass adapters in the alundum furnace tube. These Morganite tubes were filled with steel turnings, whose function it was to catalyse the cracking of the ammonia. The furnace tube, which was wound with a nichrome element, was capable of maintaining a temperature of 850°C to 900°C when carrying 6 to 7 amps., and was insulated thermally, atmospherically and electrically by teased asbestos wool in a sheet metal casing. The mixture of gases (nitrogen, hydrogen and ammonia) leaving the furnace passed through the trap E (similar in purpose to C but with the stopper leads reversed) to the washer F. The weakness of the original design of washer lay in its proneness to leakage of both water and gas - a direct result of its complicated construction. Efficient washing was obtained by using the simple four stoppered glass bottle of the type shown in Fig.1. Essentially this was an exaggerated Wolffe's bottle, the large middle stopper in the head of the bottle serving as an inlet for the gases from the cracking furnace, and exit for the washed gases by one of the other smaller openings. Periodically, the heavily ammoniated water was emptied through the lower cock of the washer and replaced by fresh water through the remaining stopper in the head. The train circuit was completed by passing the washed gases through two wash bottles containing concentrated sulphuric acid and thence through two calcium chloride towers to the bottom of the furnace proper. These last stages removed the final traces of ammonia and

Fig. 2.

Design of Apparatus for measuring the activity of Cokes in various Atmospheres.



moisture.

The construction of the high temperature furnace is shown in Fig. 2. A mild steel cylindrical casing with removable top and bottom plates sits on three equi-spaced legs bolted to the bottom plate. This plate had a central hole carrying a screwed steel tube bend from which a rubber tubing length was taken to the outlet end of the second calcium chloride drier of the cracking train to form the link between train and furnace. Over the hole in the bottom plate rested an alundum gas distributor, a device which diffused the gases to every part of the molybdenum winding. A second hole eccentrically placed to clear the distributor had a straight screwed tube inserted for the entry of one of the terminal leads of the winding. The cylindrical casing fitted into a groove in the bottom plate, and an air tight joint was made by filling this groove with asbestos cord soaked in water glass and plastering the outside of the casing at the joint with a hard setting cement mixture of china clay, ball clay and water glass.

The furnace tube was made of alundum, properly graded, and wound with 42 ft. of molybdenum wire (0.04" diam.). The free ends of the winding were attached to thick plaited nichrome wire as leads to the terminals. The winding was covered with a thickness of alundum. The tube sat in a groove in the solid top of the gas distributor, one of the leads going through the straight tube in the bottom plate, but was insulated from it by a silica sheath fitting over the plaited wire. A plug of asbestos and a covering of the cement, mentioned above, closed the free end of the steel tube to the air. Midway between the furnace tube and the casing was inserted an alundum sheath; between the sheath and the casing was a lagging of teased asbestos for thermal insulation, and between the sheath and the tube the neutral atmosphere circulated.

The top plate with a central hole surrounded by screw threaded bolts was placed in position and jointed as for the bottom plate. A third and smaller plate was fitted over the

furnace tube and bolted to the top plate by the screw threaded bolts. All joints were made as air tight as was possible by the cement mixture. The second lead was insulated from the top plate by an alundum swab. The top and bottom plates were connected through six bolted steel rods. In series with the furnace was a mobile variable resistance unit with ammeter, designed to carry 42 - 45 amps. The terminals of the furnace were connected through this resistance to the mains supply.

The atmosphere in which the experiments were conducted could only be controlled by the use of a material impermeable to gases at all temperatures up to 1600°C (alundum failed in this respect), while still retaining sufficient strength to resist collapse at these temperatures. Pythagoras, a fused high temperature porcelain, fulfilled these conditions. A tube of Pythagoras (30" x 2" I.D.) with one end closed was placed with this end in the furnace and was suspended $\frac{1}{4}$" above the top of the gas distributor from a fixture resting on the top plate of the casing. An alundum crucible was used to hold the charge of coke, and this crucible was supported on an alundum stool at such a height as to receive the maximum of heat from the furnace wall.

The open end of the Pythagoras tube had a rubber bung with a T piece insertion, one end of which was connected to a Cenco Hyvac pump and the other to one limb of a mercury manometer, graduated in millimetres. All connections were made with pressure tubing, sealed with an amyl acetate solution of celluloid.

At the higher temperatures of the furnace certain electrical disturbances were superimposed upon the normal thermoelectric effect of the thermocouple. The precise origins of this phenomenon are still indeterminate, but its effect has been nullified in the following manner. If that part of the Pythagoras tube in the hot zone of the furnace was covered on its outside with a length of molybdenum sheet (the grid), bound by molybdenum wire to the tube, the true temperature/E.M.F.

relationship of the thermocouple was preserved. Between the grid and the Pythagoras was inserted the thermocouple of tungsten/molybdenum wires, insulated from each other and from the grid by silica sheathing. The thermocouple point was adjusted on the outside of the Pythagoras to the height of the bottom of the crucible in the inside, the temperature difference in the two positions never exceeding 5°C. The E.M.F. of the couple was balanced on a Tinsley Vernier potentiometer against an E.M.F. of known value. The standardisation curve of the particular tungsten/molybdenum wires, which is a function of the state of the wire as received, was obtained by comparison with a standard chromel/alumel couple to 1000°C. For temperatures above this limit, the melting points of copper, Armco iron and the γ/δ transformation were sufficient to determine the curve of the couple. An Ayrton Mather galvanometer and scale indicated the point of balance of the couple E.M.F.

Three varieties of cokes with differing characteristics as to origin and manufacture were considered with respect to the following sequence of defined operations.

(a) Recarbonisation.

Heating the coke sample, lump or ground, in vacuo to 1400°C. Evacuating the evolved gases at the maximum temperature of the treatment, followed by cooling to 200°C under continued evacuation.

(b) Decoking of the Alundum Crucible and Stool.

Removal of the carbon deposited in the pores of the crucible and stool as a result of (a). This operation was unnecessary and was omitted with a Pythagoras crucible.

(c) Desorption.

Repetition of operation (a) with the recarbonised product of (a). This was omitted when using a Pythagoras stool and container.

(d) Oxygen Treatment.

The effect of low pressures of oxygen on (c) to 1400°C. Evacuation of the gaseous products of this controlled combustion at the maximum temperature was continued to 200°C.

(e) Nitrogen Treatment.

The effect of low pressures of nitrogen on (c) or (d) to 1400°C.

A simple graphical representation of the variation with

temperature of the gaseous pressure of the Pythagoras system in the presence of a coke charge has been found wanting in the interpretation of the behaviour of coke under the conditions (d) and (e). This is due to the many complicated factors of the blank system itself, which being incalculable have to be eliminated by a differential method of graphical construction depending upon the repeated estimation of the thermal expansion of various pressures of oxygen and/or nitrogen in the closed Pythagoras system with no coke charge. The conduct of this standardisation was as follows.

The Pythagoras tube with alundum stool and container was evacuated, tested for leakage overnight and a quantity of oxygen (or other gas) filtered in to the closed system to give a desired pressure, approximately equal to that pressure it was proposed to use in tests (d) and/or (e). The tube plus its contents were heated to 1300°C - 1400°C, the equilibrium readings of pressure being taken at arbitrary temperature intervals of 200°C to that range. The definition of equilibrium was limited for convenience to that maximum reading which after 15 minute periods did not differ from the previous reading by more than 2 mms. In all these standardisations the tube with its gaseous contents was allowed to cool overnight, and the degree of vacuum obtaining the following morning considered evidential exclusion of possible absorption, volatile emission or atmospheric leakage. Only such experiments were valid where the room temperature readings of pressure on the successive mornings of an experiment are markedly the same.

Fig. 3, curve (a), shows the typical standardisation curve of the procedure outlined above. The linear relationship of gas pressure and temperature is maintained to the highest temperatures, the only departure from the straight line (outwith experimental error) lying in the region of 0°C to 100°C, which is of comparatively minor interest. Fig. 3, curve (b), is an original graph obtained with the virgin apparatus. Its consistently higher values in the pressure scale relative to the

corresponding temperatures of curve (a) indicate the emission of moisture or other volatile matter from the fresh alundum or Pythagoras. Leakage is excluded by the constant vacuum reading of the next day. The result of annealing the Pythagoras, etc., at 1400°C under continued evacuation and repeating the standardisation is shown in Fig. 3, curve (a). During the comparatively intensive use of the apparatus under the later experimental conditions - conditions which were likely to affect the standardisation, e.g., carbon deposition, - the individual values of the points of this curve did not deviate by more than ±0.5% of the absolute value at any temperature.

The initial pressure of oxygen of Fig. 3, curve (a), (12.0 cms.) has been chosen as approximating to the partial pressure of the oxygen in the atmosphere (14.0 cms.). The standardisation has been repeated with a pressure of 45.5 cms. In Table 1 these results are shown in columns 2 and 4. The penultimate column calculates the figures of column 2 to an initial pressure of 12.0 cms., on the basis of an assumed direct proportionality. The results of the experimental determination of the thermal expansion with the lower pressure are reproduced in the final column. Comparison of the last two columns proves that the rate of change of pressure with temperature is independent of the initial pressure within wide limits of that pressure. This deduction will be used in later work in connection with the derivation of the differential curves. The gradient of these standardisation curves is higher the greater the initial pressure and this is explicable on the recognition of the lesser approximation to the ideal state of the perfect gas of the higher pressures (6). The difference, however, can be appreciated by the following figures:-

High Pressure, 45.5 cms. Gradient 0.69 mms./°C.
Low Pressure, 12.0 cms. Gradient 0.68 mms./°C.

Lastly, the standardisation curve is neither a function of the gas in the system nor of the material of the crucible or stool. The curves obtained with nitrogen or air, alundum or Pythagoras

TABLE 1.

To prove that the thermal expansion of the gas in the Pythagoras is independent of the initial pressure.

Temperature. °C.	Oxygen Pressure. cms.	Recalculation to a basis of 12.0 cms.	Observed Pressures. cms.
20	45.5	12.0	12.0
370	58.7	15.4	15.4
680	67.4	17.6	17.5
980	76.2	19.9	19.6
1280	84.5	22.2	21.8
1400	87.4	23.0	22.6

Note: Factor of conversion from column 2 to column 3 is 1.00/3.80.

TABLE 2.

Proximate Analyses, Conditions of Manufacture and Relevant Data of the Cokes used in these experiments.

Proximate Analysis.		Coke A.	Coke B.	Coke C.
Moisture.		1.0	2.0	0.4
Volatile Matter less Moisture.		0.4	0.5	0.2
Fixed Carbon.		96.7	88.7	86.1
Ash.		1.8	8.8	13.3
Maximum Coking. Temperature Range.		1120°C. 1150°C.	1140°C. 1160°C.	1180°C. 1220°C.
Coking Time (hrs.).		25	25	17
Screen Analysis (I.M.M.).	-40) +100)	61.5	38.2	-
	-100	38.4	61.7	-

Fig. 3.

To prove that the thermal expansion of the gas in the Pythagoras is independent of the initial pressure.

Curve (a) - Initial pressure 12.0cms.
Curve (b) - Virgin apparatus.
Curve (c) - Initial pressure 45.5cms. (See context).

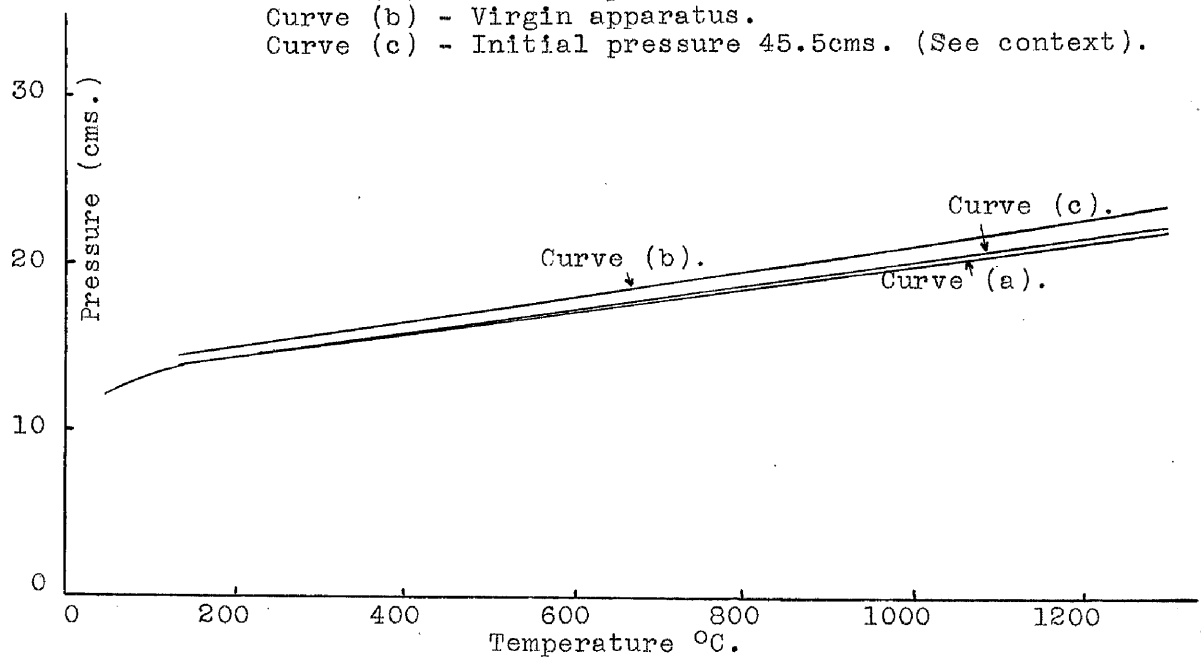
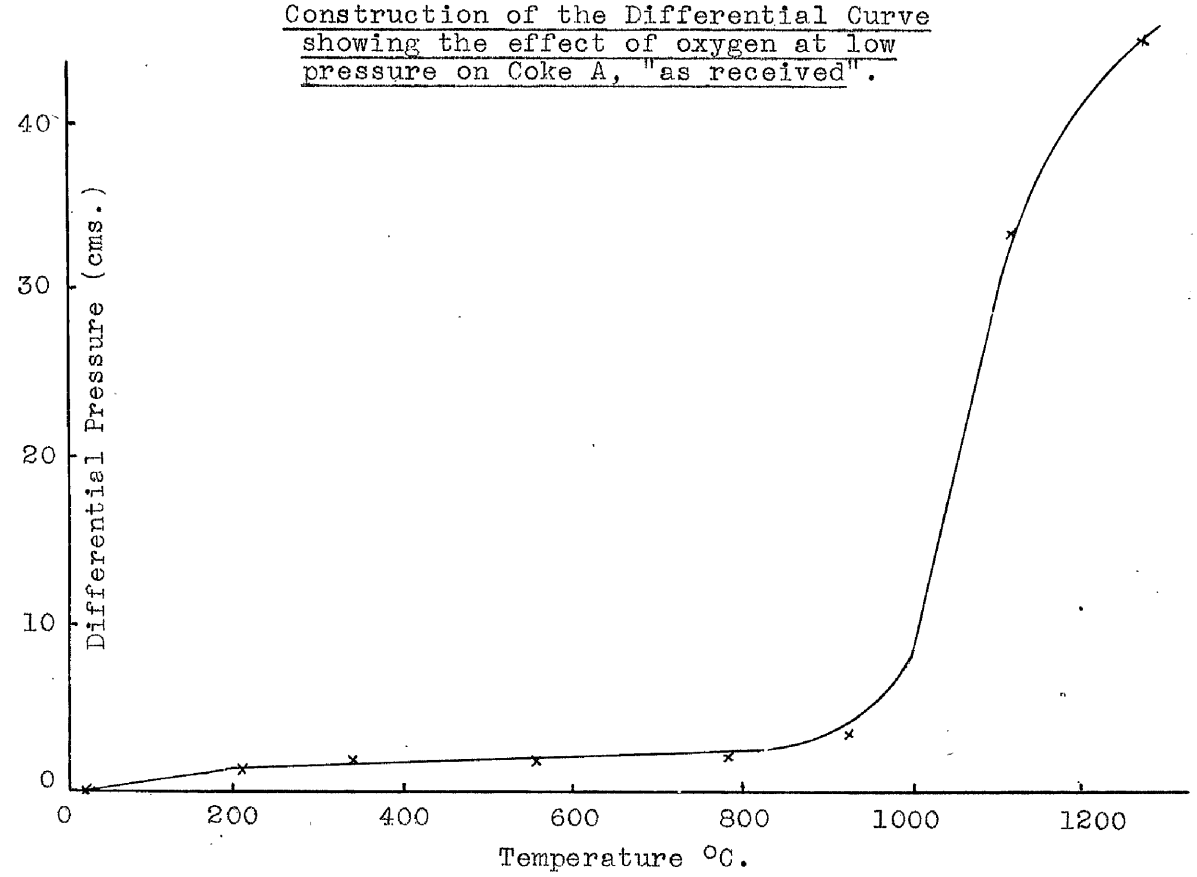


Fig. 4.

Construction of the Differential Curve showing the effect of oxygen at low pressure on Coke A, "as received".



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are identical with Fig. 3, curve (a).

The first experiments with a coke charge were attempted with the low ash coke, Coke A, used in the making of electrodes. Its analysis and the approximate conditions of its manufacture are given in Table 2. 500 grams of the coke were ground, not to specified mesh limits but rather to provide a large surface area per gram of material. The screen analysis (also given in Table 2) indicates the measure of the grinding. 5 grams of this ground coke were placed in the alundum container, the tube evacuated and oxygen to a pressure of 12.0 cms. passed into the system. Heating to 1300°C and the taking of readings were continued as for the standardisation In Table 3, as an example of the differential curve method, the results are reproduced in columns 2 and 3. Column 4 gives the corresponding readings of oxygen pressure which would have been recorded in the absence of the coke, calculated by direct proportion from Fig.3, curve (a), on the assumption of an initial pressure of 12.3 cms. as against 12.0 cms. The final column is the difference between columns 2 and 3, and this difference is assumed as being primarily due to the reactions between coke and oxygen. These differences have been plotted in Fig. 4 against the corresponding temperatures. This curve has proved to be compounded of several simultaneous reactions. There is, for example, a decomposition of the coke itself, an adsorption of oxygen, partial combustion, etc., and it is with the intention of differentiating between these that the experimental procedure (a) to (d), inclusive, mentioned previously, has been adopted.

2.25 grams of the ground coke were placed in the container, as before, and heated in vacuo to 1400°C, readings of pressure of the evolved gases being taken at definite intervals of temperature. Conditions of equilibrium were considered to have been established under the previously defined limitation. The total time for each reading thus varied from ½ hour to 1½ hours, being a function of the temperature. The higher the temperature

TABLE 3.

Construction of the Differential Curve.

Showing the effect of oxygen at low pressure on Coke A, as received.

Temperature. °C.	Gaseous Pressure. cms.	Corresponding Standard. cms.	Difference. cms.
20	12.3	12.3	-
210	15.8	14.7	+ 1.1
340	17.6	15.6	+ 2.0
560	19.2	17.2	+ 2.0
790	21.0	18.8	+ 2.2
930	23.4	19.8	+ 3.6
1120	55.2	21.1	+ 34.1
1280	68.2	22.2	+ 46.0

Note: Plotting gaseous pressure directly against temperature does not provide a satisfactory graphical construction, (see context). Instead, a differential method has been adopted. The difference between the gaseous pressure developed in the tube in the presence of the coke and the pressure developed at the same temperature in the absence of the carbonaceous material is plotted against the temperature. (See curve, Fig. 4.).

TABLE 4.

Analyses of the Gases evolved on Recarbonisation.

Gas Constituent.	Coke A. (Ground)	Coke B. (Ground)	Coke C. (Ground)	Coke B. (Dried)	Coke B. (Massive)
Carbon Dioxide.	-	-	-	-	-
Carbon Monoxide.	56.9	64.8	39.0	74.7	61.0
Oxygen.	3.6	1.6	2.1	3.2	2.3
Hydrogen.	23.6	11.3	34.0	-	35.6
Hydrocarbon as Methane.	3.4	2.9	-	3.6	-
Nitrogen as difference.	12.5	19.4	24.9	18.5	1.1

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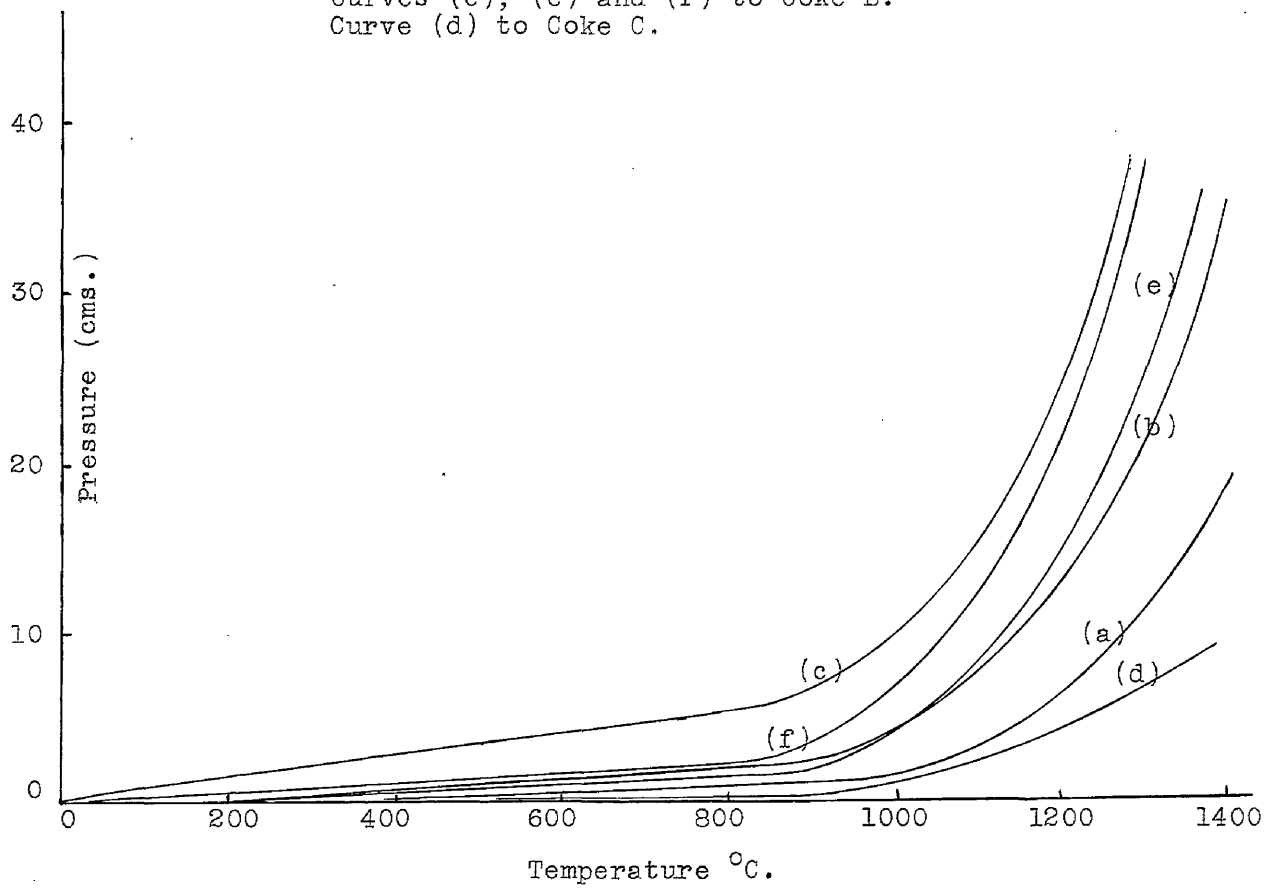
the longer the period for the attainment of equilibrium. The progress of the evolution of gas, which is a measure of the coke stability, is shown as curve (a) of Fig. 5. The gases evolved were collected at 1400°C and analysed on a Bone and Wheeler apparatus. The analysis is given in Table 4. Repeating with a 5 gram sample of the same coke, Fig. 5, curve (b), shows that the amount of gas evolved at the higher temperatures is proportional to the weight of ground coke used in the experiment. Recarbonisation of random lump samples does not provide a similar proportionality of gas evolution to coke weight. The differential method of graphical construction cannot and need not be employed in the discussion of recarbonisation. The analysis of the gas from this duplication differs negligibly from that quoted in Table 4.

In the case of Cokes A and B, the same breakdown of the coke structure is to be observed in varying proportions, accompanied probably by allotropic changes not evidenced by these experiments (7, 8), (See Chapter 3). The recarbonisation curves for these cokes are reproduced in Fig. 5, curves (c) and (d), respectively, and the analyses of the gases evolved by the separate cokes in Table 4. The considerable variations in the analyses between these three cokes are particularly noteworthy, but two further observations are deserving of mention. Firstly, it is doubtful if the figure quoted in the proximate analyses of the cokes as "volatile matter" bears any relation to the recarbonisation curves of the cokes. The usual test for volatile content is to heat the coke for 7 minutes at 925°C ± 25°C in a reducing atmosphere. According to Fig. 5. the amount of volatile matter at that temperature for Coke B is only 2% of that obtainable at 1400°C. Secondly, these curves indicate that above some temperature differing from coke to coke but constant for each coke, the coking process begins anew. For Coke A this temperature is 800°C; for Coke B, 880°C and for Coke C, 960°C. Coke above this temperature (designated the

Fig. 5.

Showing the effect of heating various cokes in vacuo.

Curves (a) and (b) refer to Coke A.
Curves (c), (e) and (f) to Coke B.
Curve (d) to Coke C.



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recarbonising temperature) virtually becomes a coal with a higher carbon content than the coal from which it was obtained originally or, alternatively, coke is a complex at a stage in an irreversible process, the beginning and ultimate end of which will be defined in Chapter 3. Its stability is to be measured by the proximity of its approach to this ultimate end, which is complete graphitisation of its organic content.

Note too, curve (e) of Fig. 5, where 5 grams of a dried sample of the ground coke B were recarbonised. The difference in the type of curve for the "as received" product (curve c) is particularly noticeable, and a comparison of the analyses of the gases on Table 4 obtained under equivalent conditions informative. The absence of hydrogen in the gases from the dried sample appears to be due to the initial drying, the evolution of moisture from the basic sample in the original recarbonisation experiment acting on the white hot coke according to the well known water-gas reaction. Fig. 5, curve (f) shows the effect of heating a random lump sample of coke B, approximate weight 5 grams (cf. curve c) and the analysis of the evolved gas on Table 4. The differences are those which would naturally be expected from a haphazard choice of a heterogeneous bulk sample.

Certain observations have also been made on the physical changes accompanying recarbonisation. Ground, the various cokes after a recarbonising treatment to 1400°C appeared uniformly duller on the surface layers, but with the underlying mass of the charge retaining its original appearance. The outer surfaces of massive samples of these cokes, however, presented after the same treatment a patchwork of distinctive areas. Some were covered with a sooty deposit, removable by scratching with a file but adhering too strongly to the under-surface of the coke to be blown off. In other parts the coke had a glittering iridescent appearance, while still other sections seemed unaffected and of the original dull grey colour. These superficial alterations may be explained by -

(α). the cracking of the volatile hydrocarbons in their passage through the intergranular spaces of the ground charge or along the microscopic cleavages of the massive samples or by carbon deposition at the outer surface from the atmosphere created by the thermal decomposition of the coke.

(β). the breakdown reaction, $2CO = CO_2 + C$.

(γ). the dissociation of those parts of the original coal structure, unaffected by the temperatures of the industrial coking but unstable at the much higher temperatures of the experiment.

The evidence for (α) is to be found in the discoloration of the alundum crucible and stool after recarbonisation of the coke charge. This phenomenon will be enlarged upon later in this chapter. The evolution of gases in itself presupposes (γ) and its effects are to be seen on the surface of massive charges in the various and progressive decompositions of the heterogeneous compounds of any coke, as mentioned above, and the high percentage of nitrogen in the evolved gases, indicative of a breakdown of the more highly resistant nitrogenous compounds (9), (See Table 4). The reaction (β) only occurs on a falling temperature, and since the gases are continually pumped off from 1400°C to room temperature, this reaction cannot be effective. As further proof of this contention, it can be stated that experiments conducted in pure carbon monoxide do not seem to affect either the coke or the crucible.

In the original experiments stages (b) and (c) were omitted after the recarbonisation process (a), which was immediately followed by (d). A determined pressure of oxygen was added to the Pythagoras system carrying the coke charge, and the corresponding equilibrium readings of pressure and temperature noted. The graphical expression of these results is to be found in the derived curve of Fig.6. The method of its deduction has already been explained, but its validity is basically dependent upon the precise knowledge of the blank standardisation at the period of combustion of the coke, and the assumption that this standardisation is unaffected by the recarbonisation is disproved by experimental determination.

Fig. 6.

Showing the effect of oxygen on recarbonised coke A.

Curve (c) refers to the dotted graph.

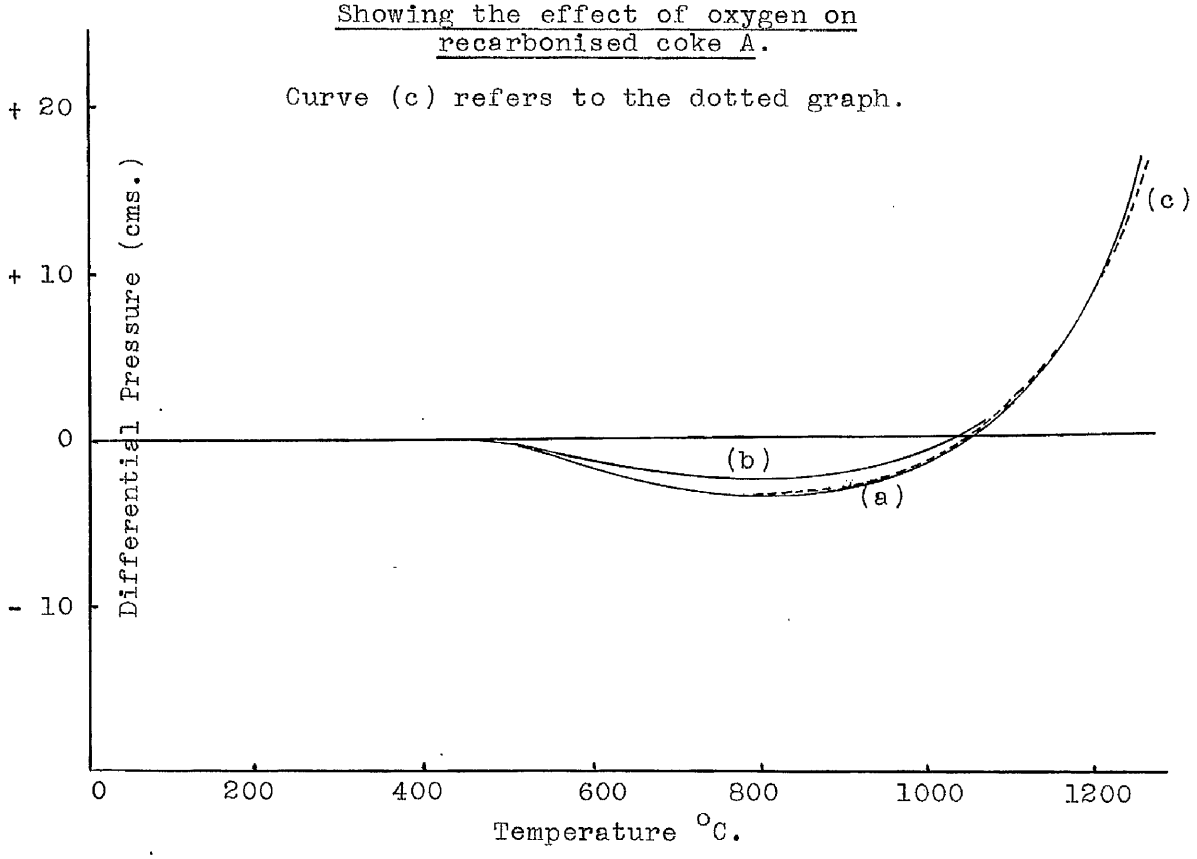
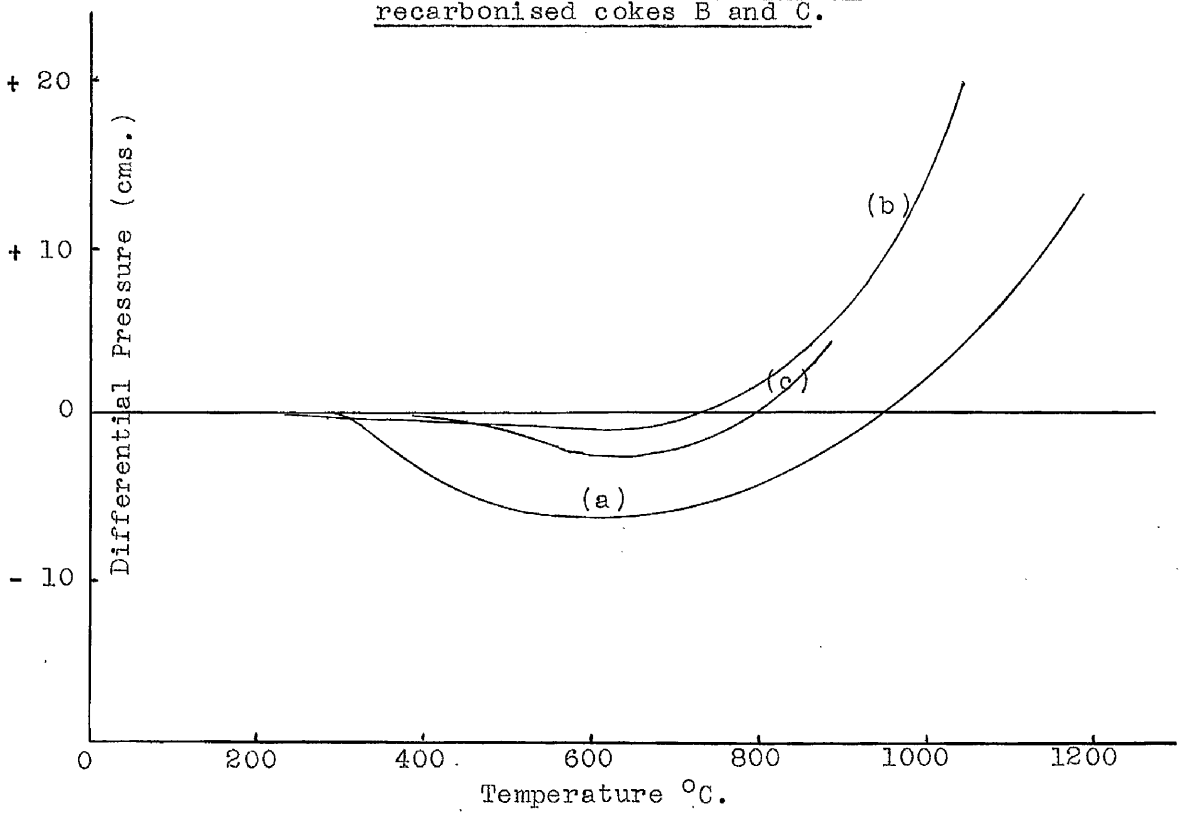


Fig. 7.

Showing the effect of oxygen on recarbonised cokes B and C.



In fact, such a blank run gave a less pronounced version of Fig. 6, curve (a), indicating the presence of carbon, or an equivalent activator. The discoloration of the crucible and stool is produced by deposition of carbon (resulting from the dissociation of the gases evolved during recarbonisation) in the pores of the alundum and to this is to be attributed the unsatisfactory null condition of the standard. By burning out the deposit previous to repeating the standardisation, the normal curve of Fig. 3, curve (a) is obtained. To do this, however, exposes the recarbonised coke to the atmosphere, which may affect the surface properties, created by recarbonisation. As a precautionary measure, this coke was reheated, therefore, to 1400°C under continued evacuation (in so far as this was necessary), a procedure which left the coke as it was virtually at the end of treatment (a), together with a standardised blank which has been proved independent of the vagaries of uncontrolled deposition. The decoking of the alundum and the desorption of the recarbonised coke, stages (b) and (c) in the sequence of these experiments, will be considered as automatically performed before attempting (d) or (e) in all further descriptions.

Returning to the recarbonised sample of ground Low Ash Coke A, Fig. 5, curve (a), the effect of oxygen (Initial Pressure = 12.0 cms.) on this coke to 1240°C is shown in Fig.6, curve (a). This curve is typical of the action of oxygen on recarbonised cokes, and will be analysed in detail before proceeding to a description of the results of other cokes under varying conditions of pressure and maximum temperature.

From room temperature to approximately 200°C, no change relative to the standard, it must be emphasised, is apparent. Between 200°C and a maximum of 830°C, there is a negative difference denoting an adsorption and/or absorption of oxygen at the surface of the coke. To 480°C this absorption is a purely mechanical effect of the open pore space of packing of the coke particles upon which is superimposed an adsorptive

surface action, which is loose in nature and easily disrupted on cooling. This is simply proved, since heating the coke to 500°C produces no permanent reduction in the value of the initial pressure when the tube is cooled to room temperature. From 500°C there is a gradual curvature to a minimum at 830°C. The essential feature of this droop is its irreversibility on cooling (cf. heating to 500°C as above). By analogy with similar phenomena (10,11,12,13), this is to be accounted for either by chemical activity at the surface of the coke or by the creation of intense adhesive (inter-atomic) forces (24). The available evidence cannot resolve this subtle distinction of the physicists, but the existence of a mooted carbon/oxygen complex, C_xO_y, (13,14.15.16), could be accepted as a compromise.

The quantitative dependence of the adsorption in this temperature region on the maximum temperature of recarbonisation, treatment after recarbonisation and particle size of the coke is illustrated by the following experiments. Referring to Fig.6, curve (a), on attaining 1240°C, the gases of the reaction were pumped off and the tube cooled. The following day the oxygen treatment was repeated and the resultant Fig.6, curve (b) obtained. Particularly noticeable is the lessened adsorption minimum of this run compared with the first. There are two possible explanations. Either the adsorptive surface loses its affinity by reason of the double heat treatment or the partial removal of the upper layers by combustion exposes less active surfaces. The degree of adsorption is also greater, the greater the surface area presented to the gas and the higher the maximum temperature of recarbonisation of the coke, assuming in the latter case that the activation of the carbon surface is affected by temperature by reason of graphitisation or decomposition. Both these statements are to be accepted by the evidence of curves (a) and (c) of Fig.7. Fig.7, curve (a) shows the effect of oxygen on ground recarbonised coke B and Fig.7, curve (b) on Coke C. This latter was obtained when using a

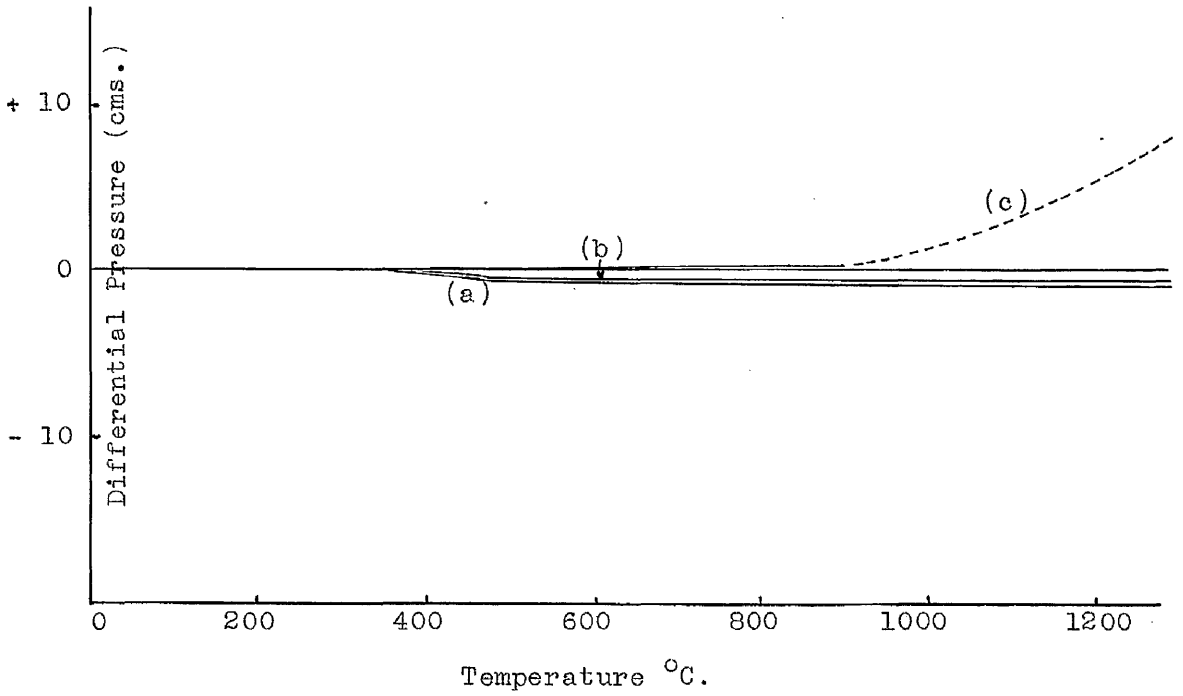
Pythagoras crucible and stool and it is to be remarked that the adsorption is very much less pronounced than in previous cases. This is a peculiarity of the coke and not a function of the container, as duplication of the experiment in an alundum container proves. The difference in the adsorptive capacity between Coke A and Coke B after recarbonisation to 1410°C may be due to the difference in the degree of fineness to which they have been ground or a difference inherent in the cokes themselves. That particle size is a vital factor in determining the extent of the adsorption can be shown by a comparison of Fig. 7, curve (a) with Fig. 7, curve (c), which is the oxygen differential curve for recarbonised massive coke B. It is questionable, however, if comparison of these two curves is really valid. The analyses of the gases obtained on recarbonisation of the ground and solid samples (see Table 4) indicate a radical difference in the composition of the charges. The effect of doubling the pressure of oxygen is shown in Fig. 7 for the case of Coke A. Its coincidence with the curve for the lower pressure shows (see below) that, although there is insufficient oxygen for the complete combustion of the coke charge, there is a sufficiency to satisfy the adsorptive capacity of the coke and that this adsorption is limited to the surface layers to a definite molecular thickness (17).

To complete the survey of the typical oxygen curve, it must not be assumed that the change from the negative to positive gradient of the curve in the region of the minimum is a discontinuous process resulting in the formation of carbon monoxide. There may be atomic changes on the surface of the coke of the adsorbed gas, which would not affect the pressure readings, but which are necessary preliminaries to the formation of carbon monoxide. Above this maximum adsorption, there is an evolution of monoxide and dioxide in indefinite proportions. These experiments with oxygen provide one of the finest examples of consecutive reactions of the type -

$$\text{Carbon} + \text{Oxygen} \rightarrow \underset{\text{(adsorption)}}{\text{Carbon/Oxygen complex}} \rightarrow \text{Carbon } \begin{matrix}\text{Mon}\\ \text{Di}\end{matrix}\text{oxide, (18),}$$

Fig. 8.

Showing the effect of Nitrogen on recarbonised cokes.



where the intermediate stage, the formation of the complex, is a necessary precedent to the chemical reaction, $2C + O_2 = 2CO$ or $C + O_2 = CO_2$.

The cokes after the oxygen treatment were heated in an atmosphere of nitrogen providing the gaseous products of the previous combustion were continually evacuated from the maximum temperature to 200°C. The differential curve for operation (e) after (d) is shown in Fig. 8, curve (a), and in the same figure curve (b), the effect of performing the nitrogen treatment after recarbonisation without the intermediate oxygen treatment. With nitrogen as the gaseous medium, the absorptive and adsorptive effects are to be seen on a small scale, while the formation of any nitride can be discounted by reason of the complete absence of the minimum, which was a feature of the oxygen curve. The cylinder nitrogen was freed from oxygen by passing the gas through pyrogallic acid before entering the Pythagoras tube. The following nitrogen experiments indicate the intensity of the physico-chemical forces of adsorption and show the effect of temperature in diminishing their influence. Ground Coke A after evacuation at 1080°C in the experiment of Fig. 6, curve (b), was used in a further treatment with nitrogen to 900°C. The differential curve of this operation is shown in Fig. 8, curve (c). The gases resulting from such an experiment analysed only traces of carbon monoxide and oxygen. The bulk appeared to be nitrogen. In a similar experiment the heating in nitrogen was continued to 1400°C. The readings of pressure and temperature were identical to 910°C, but above this temperature the results are as shown in the dotted part of the curve of Fig. 8, curve (c), and the gas evolved at 1400°C had a monoxide content of 33.8%. Such a gas could only be evolved if the oxygen and/or carbon monoxide adsorbed in the previous two experiments were removed on heating to a temperature above the maximum temperature of the previous two experiments with oxygen or, alternatively, above a temperature at which the carbon/oxygen reaction takes place.

The possibility of dispensing with operations (b) and (c), the series of firings between experiments, led to a search for materials without a tendency to activate carbon deposition. The use of a platinum suspension and crucible was obviated by the embrittlement of that material during recarbonisation. Its known adsorptive powers would, no doubt, also have militated against its use. One suggestive feature of these experiments was based on the observation that the Pythagoras tube in which all the experimental work had been done, had shown no visible experimental effects of any intervention in the coke reactions. That this is so has been proved conclusively by the coincidence of the tube standardisations before and after recarbonisation without intermediate firing of the Pythagoras tube. Nor is there any sign of carbon deposition on the side of the tube. The alundum crucible and stool were, therefore, replaced by Pythagoras ones, which were used exclusively in the experiments with Coke C. With the elimination of the "greying" of the container the experimental series, recarbonisation, oxygen and nitrogen treatments, can be carried out without removing the coke from the tube.

The conclusions of this chapter furnish clues to the probable mechanism of coke combustion, but they find limited applicability to the industrial conditions of coke usage. The method of this part of the research restricts the scope of development to the measurement of equilibrium conditions. This knowledge is important only in so far as it shows the ultimate tendency of any coke/oxygen activity, and Chapter 2 concentrates attention on a possible solution of the quantitative measurement of this tendency to equilibrium, the reaction velocity of the heterogeneous system coke/oxygen.

CHAPTER TWO.

The quantitative measurement of combustibility.

In a survey of the work of the Coke Research Committees, Evans and Ridgion state that "combustibility requires precise definition and the whole question of the combustion of carbon at low and high temperatures requires further analysis"(3). That some qualitative definition of combustibility must necessarily precede a discussion of its measurement is obvious, and,pertinent to common usage, the term combustibility will define the rate of reaction of coke with air. The distinction between air as the gaseous medium of combustibility and oxygen is intentional, since no proof has as yet been tendered that the role of nitrogen in combustion is confined to dilution of the active reactant, oxygen.

The method for measuring combustibility is essentially a continuous weighing of a massive coke sample at constant temperature and under controlled air supply. An attempt on somewhat similar principles has been reported by M. Mayers, (19,20,21). The apparatus designed to determine combustibility quantitatively is the high temperature furnace of Fig. 2 modified for the new experimental conditions as illustrated in Fig. 9. The bottom plate of the furnace casing was reamed centrally to allow the Pythagoras tube, now open at both ends, to protrude below as well as above the casing. This involved positional alterations of the entry tubes for the train gases and winding lead, besides requiring a reconstructed gas distributor in the form of a hollow, channelled, truncated cone. The Pythagoras tube was held vertically in the furnace tube under the controlled pressure of the shoulder screws of the gripping device of Fig. 9, and danger from slip was minimised by cementing tube and bottom plate. The insulation of the terminal lead, electrical connections, train arrangements and safeguards for the exclusion of air to the winding were as described in the previous chapter.

The coke was suspended from the arm of an assay balance

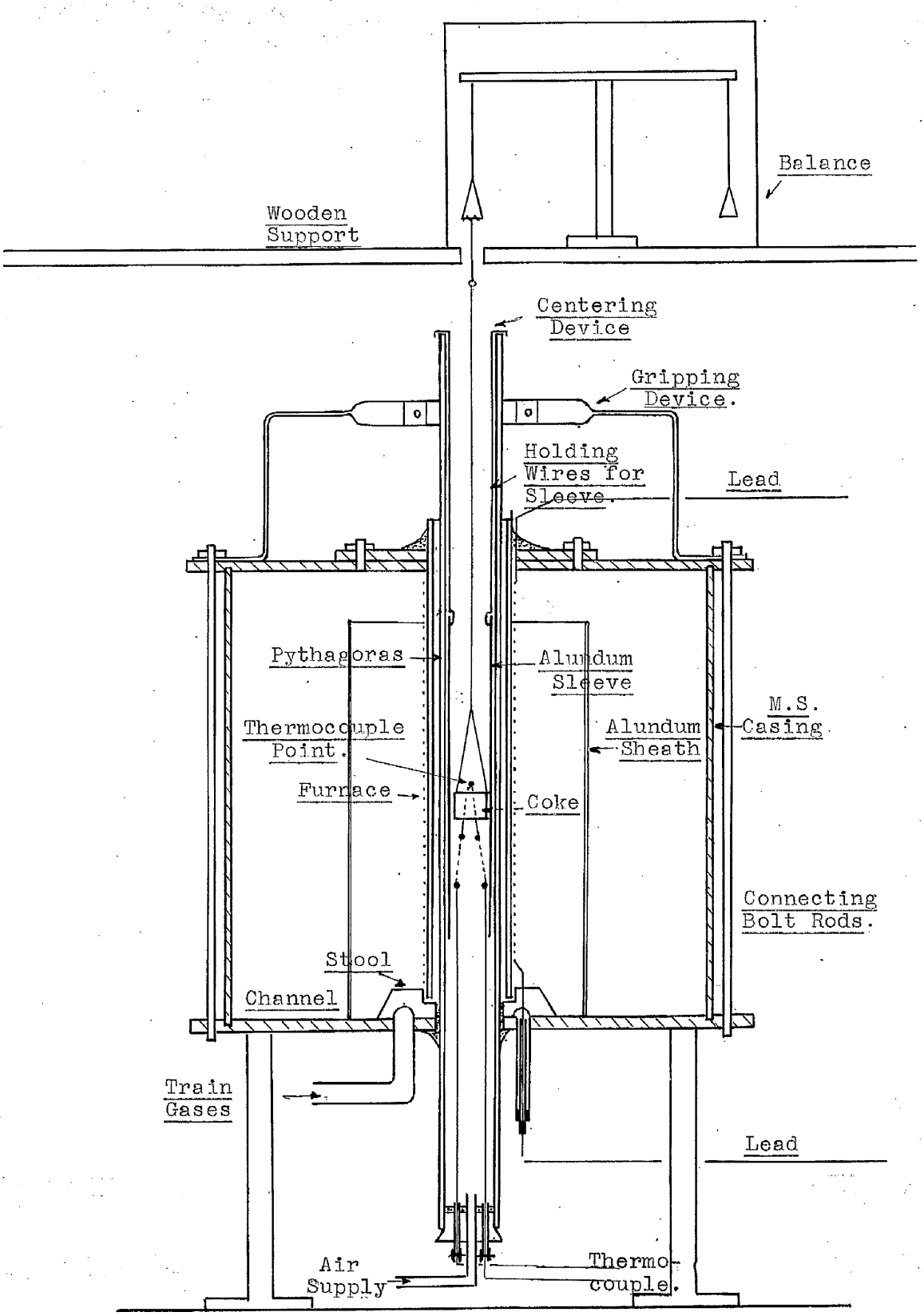


Fig. 9

Design for Combustibility Test.

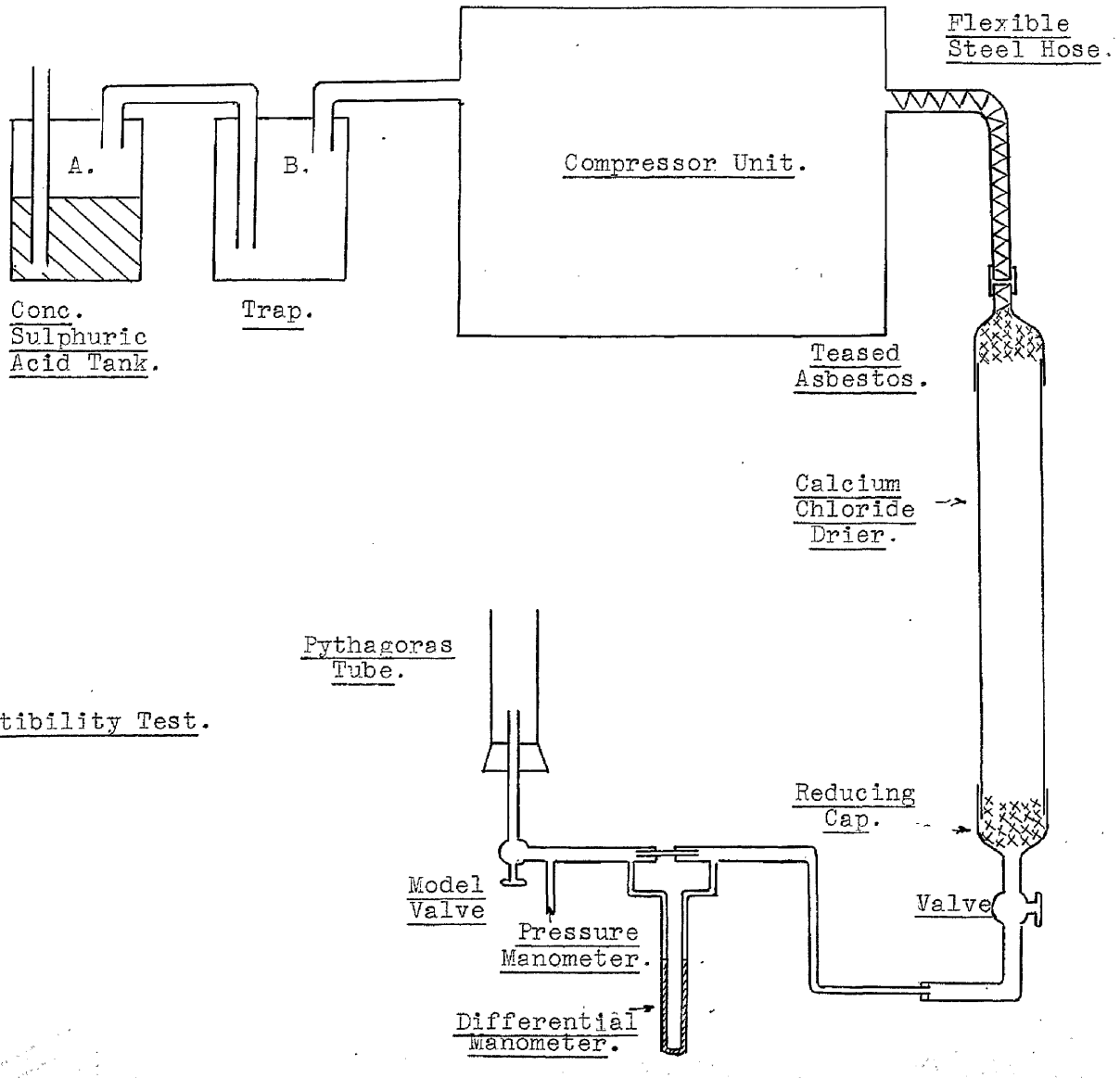


Fig. 10.

Air Circuit for Combustibility Test.

by a hook and eye arrangement of two lengths of nichrome wire of fixed length. A spoked ring on top of the Pythagoras tube centred the suspension for free movement.

In the preliminary trial experiments, the air supply for combustion was the natural draught induced by the chimney effect of the hot Pythagoras tube. For precision work such a source of draught suffered from three defects.

(1). The rate of updraught varied with the temperature of the furnace. No true comparison of the combustibilities at different temperatures was possible therefore.

(2). The amount of air induced, and

(3). The pressure of the air draught did not approximate sufficiently to the conditions of air blast in the blast furnace.

The arrangements for the maintenance of a supply of air at constant rates and pressure within the practical limits of this work are shown in Fig. 10. Experimental inconsistencies (see later) required that previous to compression the air should be dried. This was achieved in tank A, which was half filled with concentrated sulphuric acid, and from which the air was drawn into the compressor through the empty tank trap B. The compressor itself was electrically driven, single acting and water cooled. After compression the air passed through the length of 2½ in. steam pipe packed with calcium chloride. The efficacy of the drying arrangements can be judged from the fact that, excepting 3 ins. at the inlet end, the desiccating agent even after six months continual use preserved its solid appearance.

The circuit was continued from the drier to a differential manometer via a controlling wheel valve. This manometer had been constructed on the Venturi meter principle, i.e., the difference in pressure between the ends of a constriction placed parallel to the air stream is a function of the rate of air flow. The choice of jet was fixed by the following considerations.

(1). The required quantity of air must pass freely through the constricted passage at the working pressure.

(2). With the passage of the required quantity, the scale reading should be a maximum and at that part of the scale where the change of reading was at its most sensitive.

The method of calibration of the manometer will be described later.

The air was finally brought to the bottom of the Pythagoras tube through a model steam valve. Besides the injector tube soldered to this valve, there was, in parallel with the main stream, a connection to a mercury pressure manometer. The outlet tube was inserted centrally in a rubber bung fitted to the bottom of the Pythagoras, the blast thus entering the furnace vertically. Exposure of the rubber to radiant heat from the hot zone of the furnace and charring due to occasional falls of burning coke led to the substitution of an asbestos stopper. The poor resilience of this material prevented air tightness however. The asbestos bung was, therefore, halved transversely and used as a pad surmounting the rubber. The combination of resilience and non-inflammability gave such a fitting a permanence in contrast to the repeated renewals required with the simple rubber stopper.

The suspension of the thermocouple of platinum/platinum-rhodium in the furnace was effected as follows. A thin walled alundum tube (13 ins. long) was made a sliding fit for the Pythagoras. This sleeve was supported from the rim of the Pythagoras by two nichrome wires hooked near the top of the alundum tube. The couple point was inserted in the apex of the triangular arrangement of holes drilled in the sleeve, and each wire was threaded through one of the remaining holes, as shown in Fig. 9. These wires were covered with thin quill silica sheathing as a protection against breakage due to embrittlement. This was traced to floating particles of ferric ash dislodged from the burnt coke settling on the previously bared wires and, under repeated reheatings, forming a brittle iron/platinum alloy. The thermocouple wires were finally drawn through two glass lengths fitted in the bung. These tubes were

covered with rubber tubing, which,when clipped, sealed the furnace effectively from all ingress (or loss) of air, other than that intentially blown into the furnace. The free ends of the couple were connected to the potentiometer. The thermocouple point lay 3/8 ins. above (and of course to the side of) the top surface of the coke. The choice of this particular position was a compromise between localising embrittlement to the couple point and maintaining a true temperature coincidence between coke and thermocouple during experiment. The average temperature of the air entering the furnace is given in Table 5. The chilling effect on an ill-placed thermocouple is obvious. The difference in temperature between the coke sample and the relatively displaced thermocouple is reproduced in Table 5a for several temperatures.

The success, or otherwise, of the test depends primarily upon the proper preparation of the coke sample for combustion. The standard test piece has been arbitrarily fixed as a geometric cylinder, the dimensions of which have been determined in fulfilment of the following criteria.

(1). The sample should be as large as possible.

(2). The diameter of the alundum sleeve fixed an upper limit to the diameter of the coke sample. The coke must not touch the wall of the sleeve before or during weighing.

(3). The sample, if too long, will not be evenly heated, since the zone of even temperature is limited. Further restriction on the maximum length of coke procurable was due to (4).

(4). Random sampling of the bulk sample of coke does not admit of large pieces being obtained suitable for grinding. Such a block was particularly liable to shatter along hidden inside fractures.

Practical considerations of the above factors have resulted in the adoption of a standard test piece of 1 in. diameter and 1 1/8 ins. long throughout this work, unless otherwise stated. The effect of such an artificial limitation of the dimensions on the combustibility of any coke will be shown later in this chapter. While the weight of such a standard piece varied between coke and coke, for any one type of coke the weight

TABLE 5.

Showing the average temperature of the air entering the furnace.

Point where temperature is taken.	Temperature. °C.
At compressor tank.	21.5
At outlet of drier.	18.8
Before entering furnace.	18.2

TABLE 5(a).

Relation between coke temperature and temperature recorded by thermocouple (No air stream).

Coke Temperature. °C.	Thermocouple Reading. °C.
707	704
844	840
940	937
1040	1035
1160	1155

remained sensibly constant to within ± 0.15 grams. A hollow axis was drilled through the centre of the cylinder (32 S.W.G.), and a final grinding was made to bring the coke weight within the above weight limit. Where the weight of the standard sample was found to differ considerably from the average, a corresponding variation in the "combustibility figure" was also observed.

The type of suspension for the coke depended upon the proposed temperature of combustion. For the higher temperatures to 1500°C, this took the form of a crook of silica sheathing bound by asbestos cord to a length of nichrome wire. The total length of the suspension was arranged to have the upper coke surface at 3/8 ins. below the level of the thermocouple point.

The conduct of a typical combustibility experiment was as follows. The compressor was started up and, by manipulation of the large wheel valve at the outlet end of the drier and the smaller steam valve located at the bottom of the furnace, the required conditions of air rate and pressure, as recorded on the differential and pressure manometers, were obtained. Only the large valve was then completely shut off, but the setting of the small furnace valve was maintained. The suspension was balanced by thin lead sheet, and then removed, fitted with the coke sample (the wire/silica joint was remade with the same length of asbestos string each time) and lowered slowly into the furnace, when this was at or about the temperature at which the experiment was to be conducted. The furnace temperature dropped rapidly at first and a black band, indicating the zone of heat extraction by the cold coke, appeared on the wall of the sleeve. The equalisation of temperature between coke and thermocouple was considered effected when wall and coke became indistinguishable. The coke was centred in the furnace and the wall temperature allowed to rise 0.20 millivolts (+ 20°C), above the proposed working temperature.

The large air valve was opened until the pressure manometer recorded the working pressure of the entering air blast.

The fixed setting of the small furnace valve naturally passed the requisite rate of air already decided upon. The temperature dropped 0.2 mv. when the blast first entered. With the original weight of the sample about 0.7 gms. heavier than the weight at which readings of time were taken, this interval was used to allow the operator to adjust finally the air rate, pressure and temperature conditions in the furnace. Thereafter, the time taken to balance the coke at 0.5 grams intervals was observed. This was continued until the ash began to break up, which occurred usually after 80% of the coke sample had been burnt off. During the experiment the temperature was not allowed to vary more than ± 0.1 mv. (approx. 10°C) after the initial transient conditions of temperature fluctuations in the furnace had subsided. On finishing an experiment the coke piece was broken and examined. The suspension was reweighed to estimate the loss due to devitrification of the silica rod, which varied between 0.01 to 0.03 gms. according to the temperature of the experiment.

The original trial experiments were responsible for one important experimental modification. For any one coke, the result of a combustibility test at any temperature could be duplicated with reasonable accuracy, provided both experiments were done in immediate succession. A repetition at some later date, however, showed variable inconsistency outside the self-imposed experimental limits of accuracy. A redetermination of this later duplicate on the same day gave sensibly constant results, and this pointed to some disturbing factor, which operated unsystematically from day to day. This variable was traced to the moisture in the atmosphere (22), eliminated by the insertion of the tank of concentrated sulphuric acid on the precompression side of the air circuit. The original design of the apparatus relied only on the calcium chloride drier, which after a very few runs was found to be waterlogged. Reference has already been made to the success attendant upon this alteration, and a further measure of this success is to be

found in the constancy of duplication of any result after any interval. As to the error between duplicate results, this may be said to lie within ± 2% of the total time taken for the experiment, the lower the temperature the greater the error. If this figure was exceeded, a third repetition was made, although in fact this was rarely necessary.

Under these conditions, the combustibility test has been used with 7 varieties of industrial cokes, a manufactured graphite and two anthracitic coals at temperature intervals between ignition and 1500°C. The proximate analyses of these carbonaceous materials with the exception of the 2 anthracites (to be considered separately) are listed in Table 6. It is impossible and unnecessary to discuss every curve of these materials, but a few general considerations, which ultimately led to the final mathematical presentation of the results, will show the method by which these results were co-ordinated. The pencil of curves of Figs. 11 and 12 illustrate graphically on different scales the behaviour of Coke G and the Morgan Crucible Co's. Manufactured Graphite under the specified conditions of combustion. These materials have been taken as representative of the complete experimental work of this section. In Figs. 11 and 12 the graphs have been plotted to show directly the relation between time and weight, while in Figs. 13 and 14 these co-ordinates are replaced by log. weight and time.

It will be seen immediately that, while the curves relating weight and time do not admit of an obvious mathematical analysis, they do exhibit certain general properties.

(1). The curves tend to run asymptotically to the time axis, where the ordinate of the weight equals the weight of the ash in the coke sample. Practically, of course, the ash breaks off before this stage is reached, but estimates of the percentage ash in the coke have been made from these curves and these agree approximately with the analysed value of the ash content.

(2). The curves more nearly approach the weight axis as the temperature increases, i.e., the rate of combustion increases with increase in temperature.

(3). At the higher temperatures, 1250°C and above, the initial part of the curve is approximately a straight line. This direct dependence may be useful in the

Fig. 11.

Curve showing change of weight of Coke G with time during combustion.

Note: Rate of air supply for these experiments is 59.9 gms./min.

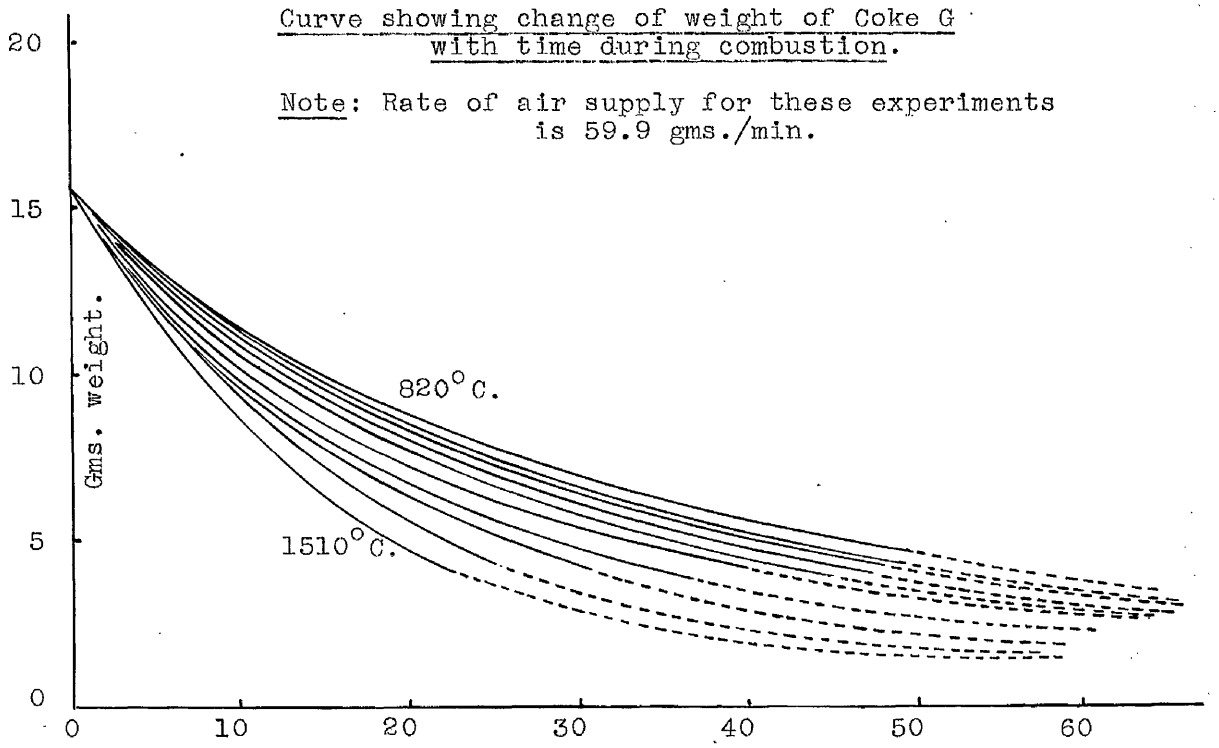


Fig. 12.

Curve showing change of weight of graphite with time during combustion.

Note: Rate of air supply for these experiments is 59.9 gms./min.

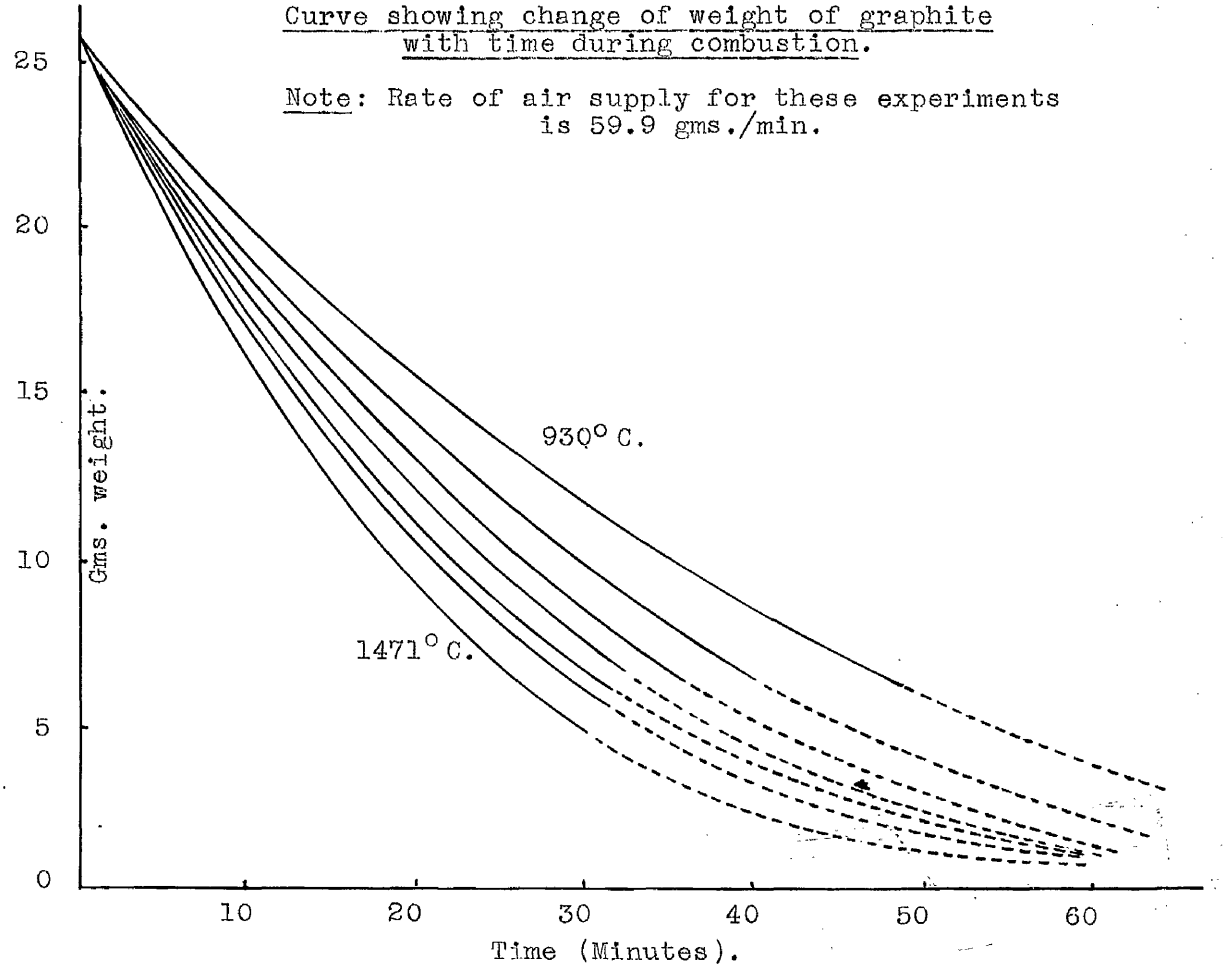


Figure on Curve denotes temperature of Combustion.

simplification of blast furnace estimates of the rate of combustion, even although the rest of the curve does not bear out this early relationship.

The measurement of the curvature differences as in Figs. 11 and 12 is complicated and unworkable. The change in co-ordinate to log. weight and time of Figs. 13 and 14 was based on a supposed similarity to the exponential curve, $y = ae^{-bx}$. This equation can be expressed alternatively as $\log_e y = -bx + C$, the conversion permitting a linear construction of the relationship between the variables with its attendant simplification over the original form of the expression. That such an assumption has a seeming basis in fact is shown by the curves of Fig. 13, and this is borne out by the curves for all the other cokes given in Table 6. The two exceptions are those for manufactured graphite and the carbonaceous briquette. Hence on an empirical choice of a possible mathematical relationship,

$$W = Ae^{-kt} \quad \text{-----} \quad (1).$$

where W = weight of the specimen in grams at any time, t minutes. The choice of units is arbitrary.

Eqn. (1) may be transformed

$$\log_e W = -kt + C \quad \text{-----} \quad (2).$$

where $C = \log_e A$ = constant.

Differentiating eqn. (2)

$$\frac{d(\log_e W)}{dt} = -k$$

or

$$\frac{1}{W} \cdot \frac{dW}{dt} = -k$$

or

$$\frac{dW}{dt} = -kW \quad \text{-----} \quad (3). \qquad (23).$$

But by the definition expressed at the beginning of this chapter, the term $\frac{dW}{dt}$ is the mathematical expression of combustibility, and this by eqn. 3 has been shown to be proportional to the weight of the reacting substance. Eqn. 1 is typical of a monomolecular reaction (15), i.e., a reaction whose rate at any instant is determined by the concentration of the reacting substances, and by eqn. 3 concentration and weight would appear to be interchangeable terms. It is important to realise that the form of graphical construction of eqn. 2 was used for the dura-

Fig. 13.

Log. Weight/Time Curves for Coke G.

Note - Rate of air supply for these experiments is 59.9 gms./min.

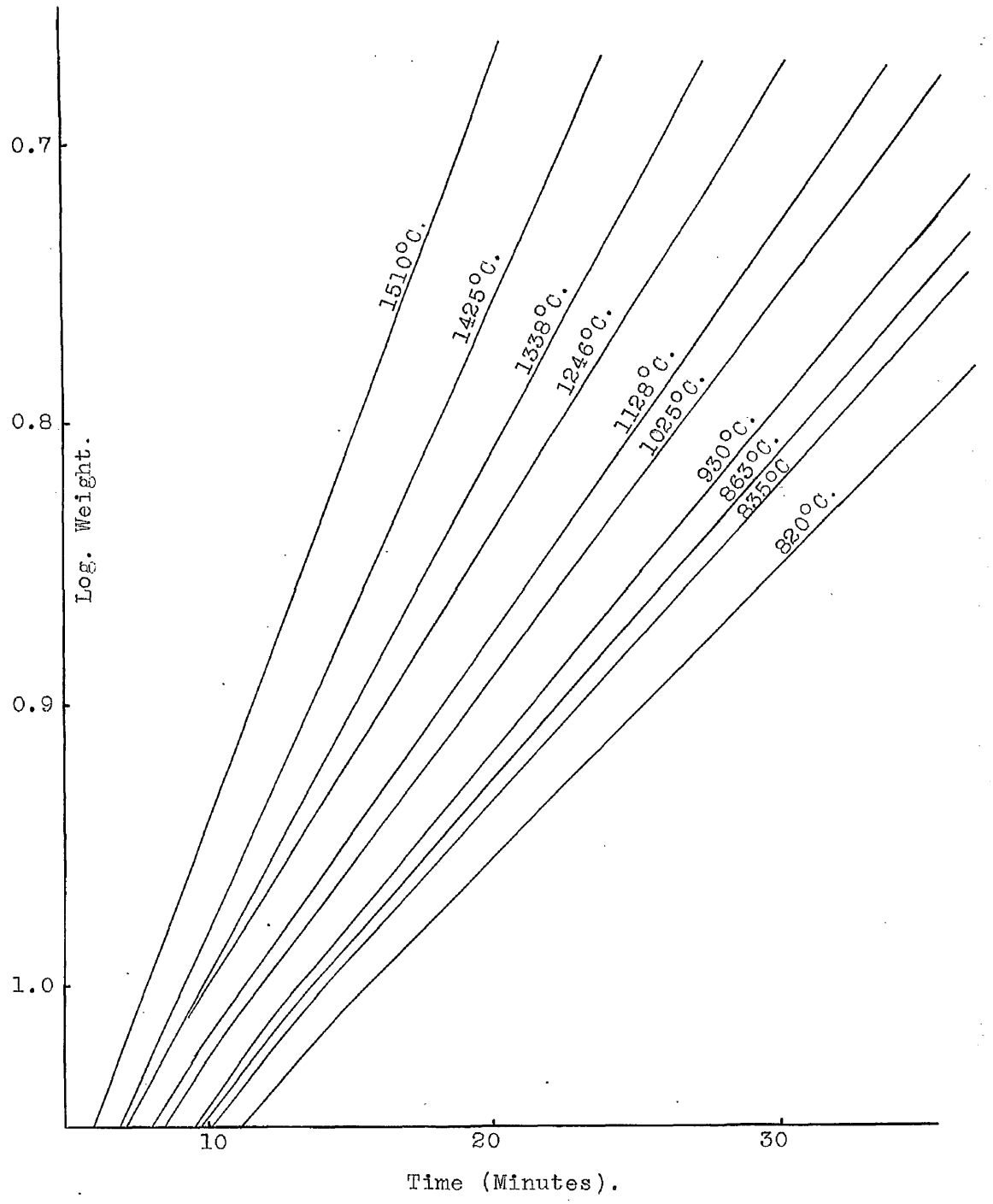


Figure on Curve denotes Temperature of Combustion.

Fig. 14.

Log. Weight/Time Curves for Graphite.

Note - Rate of air supply for these experiments is 59.9 gms./min.

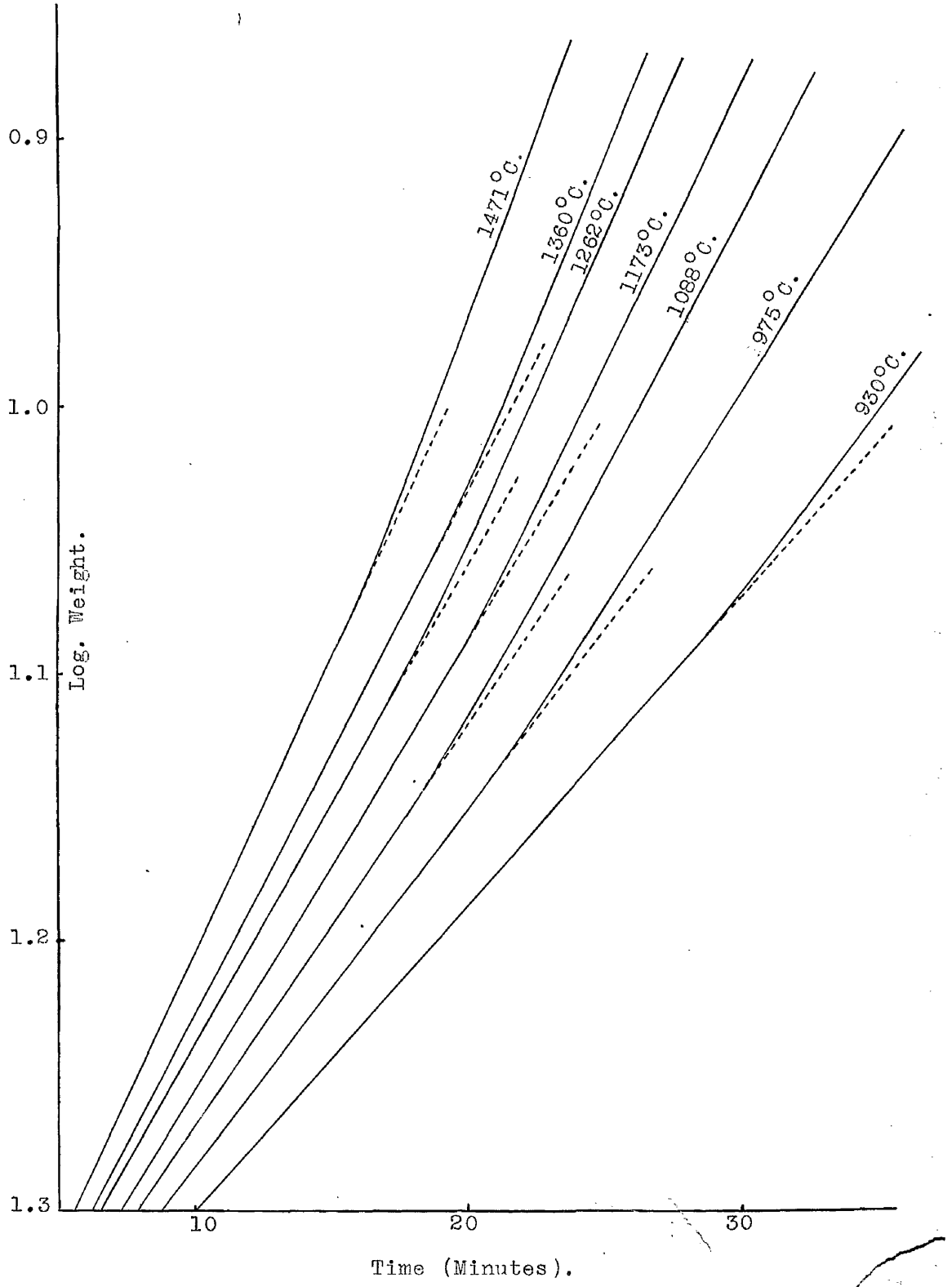


Figure on Curve denotes Temperature of Combustion.

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tion of the experimental estimation of combustibility of the cokes, as a means of defining quantitatively the differences in combustibility of the various fuels. Whatever slight deviation from the straight any particular curve may have shown could be attributed to possible "experimental error" with justification. (This statement excepts the initial deviation at the start of the experiment which will be referred to later). In the two exceptional cases quoted above such an explanation was not possible, and later became completely indefensible as further "exceptional" data accumulated. The final mathematical treatment as a substitute for the logarithmic theory is explained below.

In heterogeneous reactions as between a solid phase and a gas (24), it is generally assumed that the surface area exposed to the gas is a determining factor in the rate of the reaction; and the term "surface area" includes the very irregular surface, cracks and microscopic fissures accessible to the reactant. Consider, therefore, an irregularly shaped body of coke with such a surface as shown in the accompanying diagram, Fig. 15. By a geometrical thereom, the weight W of the specimen is proportional to the cube of any of its linear dimensions, (L_1,L_2, etc.), and the surface area A to the square of the chosen linear dimension. Mathematically,

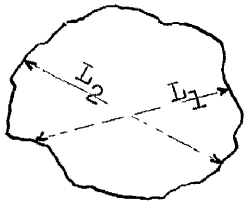
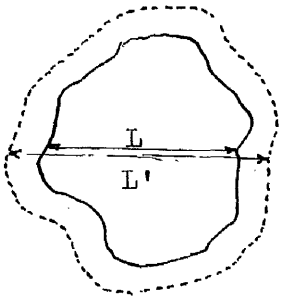


Fig. 15.

$$W \alpha L^3$$

and $$A \alpha L^2$$

from which $$A \alpha W^{2/3}. \text{ -----(1).}$$



Let the chemical reaction between coke and air proceed at this surface for a time t in such a way that the original volumetric outline is preserved in miniature as the surface decreases. This proviso is the characteristic condition of the process of combustion and will be amplified later.

The total weight of the sample W comprises -

(a). the weight of the still unburnt coke, which is represented in Fig. 15 by that part of the diagram within the unbroken outline, and

(b). the weight of the ash layer resulting from combustion during time t.

If L' and L be similar linear dimensions of the coke at zero time and time t, respectively, and D and D' the weight of unit volume of the coke and ash, then by (a) and (b)

$$W = M(DL^3 + D'(L'^3 - L^3))$$

i.e., $$W = M(D - D')L^3 + MD'L'^3$$

or $$W = aL^3 + b \quad \text{----------(2)}$$

where a is a constant equal to $M(D - D')$ and b is also a constant equal to the weight of the ash in the original specimen.

Combining (1) and (2), thus eliminating L,

$$A \propto \frac{(W - b)^{2/3}}{(a)} \quad \text{----------(3).}$$

At this stage let us assume that the rate of the reaction depends upon the surface area exposed to the air, then

$$-\frac{dW}{dt} \propto A$$

$$\propto \frac{(W - b)^{2/3}}{a} \quad \text{------ from (3).}$$

Hence by integration,

$$(W - b)^{1/3} = -kt + C \quad \text{--------(4),}$$

or, alternatively, eqn. 3 may be expressed,

$$\frac{d(W - b)^{1/3}}{dt} \text{ is a constant.--------(5).}$$

The linear relationship of (4) or the gradient constancy of (5) have been substantiated by the several hundred coke combustions performed in the manner of this test. The log. weight/time curves of Figs. 13 and 14 have been redrawn to the new scale co-ordinates to illustrate the universality of the cube root relationship, even in respect of exceptions to previous mathematical laws. While recognising the negative character of the gradient of (5), for convenience the curves are plotted as shown and the positive gradient of the acute angle between the time axis and the curve used as a measure of the combustibility

Fig. 16.

Combustibility Curves for Coke G.

Note - Rate of air supply for these experiments is 59.9 gms./min.

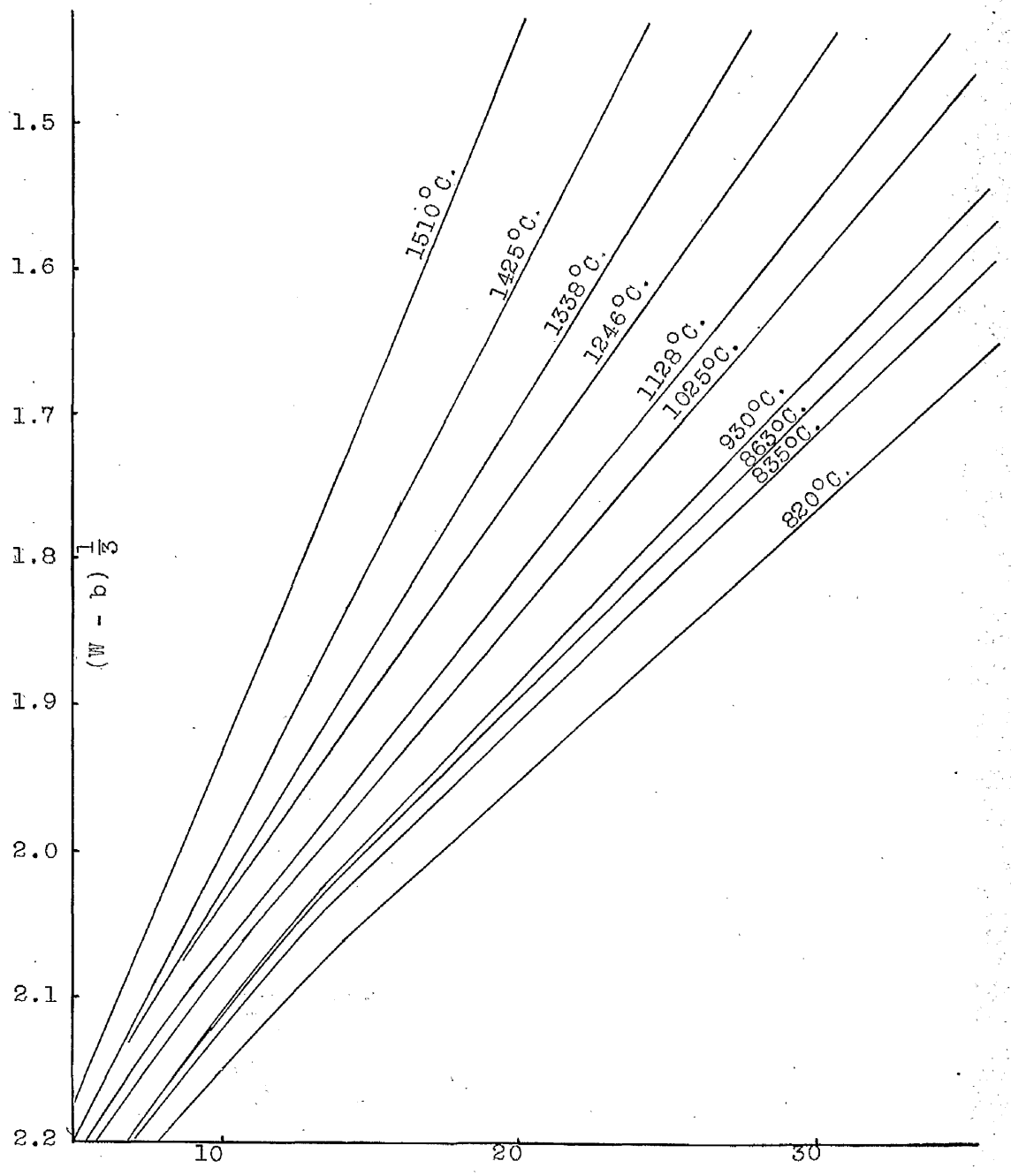


Figure on Curve denotes Temperature of Combustion.

Fig. 17.

Combustibility Curves for Graphite.

Note - Rate of air supply for these experiments is 59.9 gms./min.

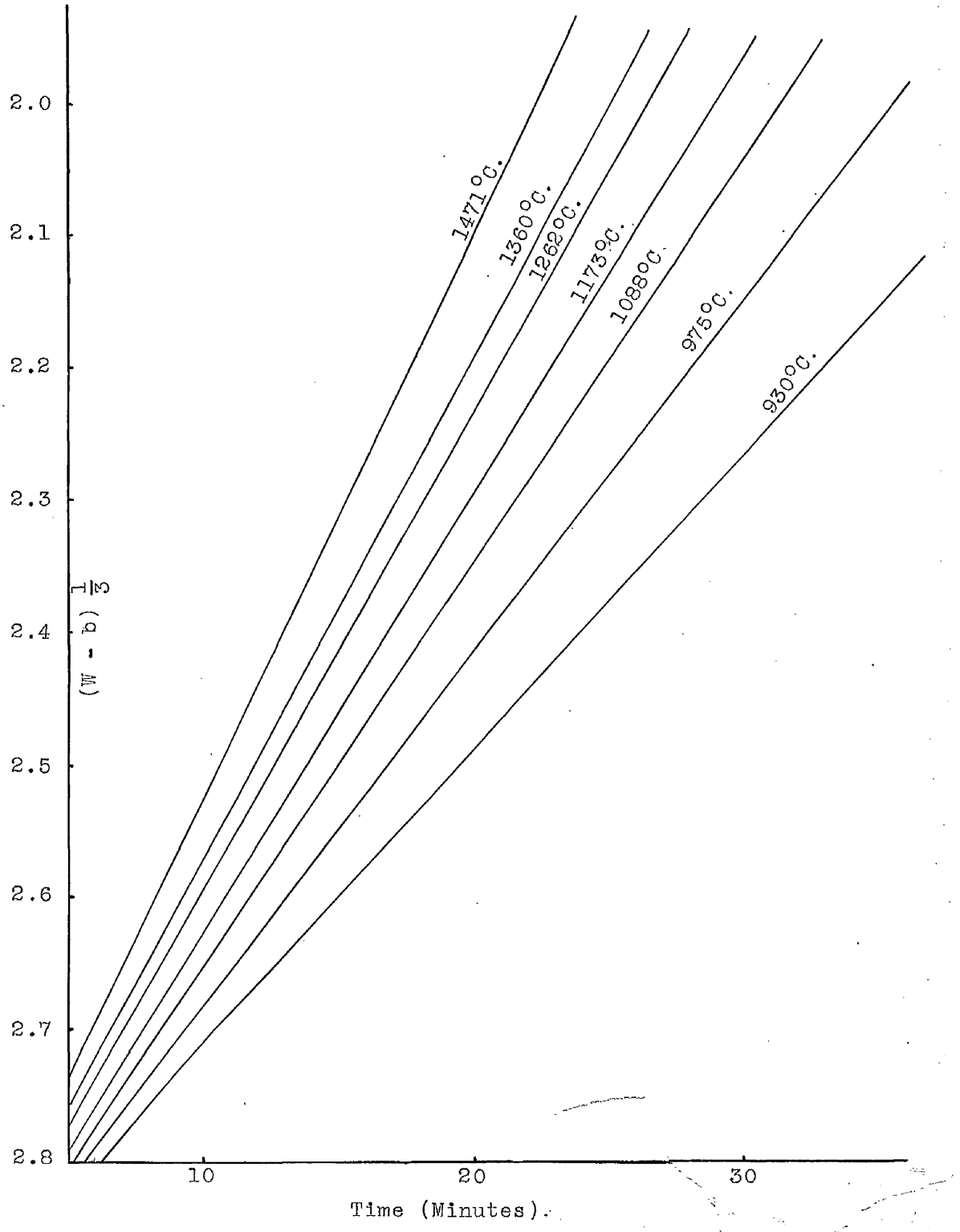


Figure on Curve denotes Temperature of Combustion.

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under the recorded conditions of temperature and air supply. The units chosen are gram-$^{1/3}$minutes and the noted value of the gradient is 100 times the real value, thus preventing confusion by the use of too many zeros. These gradients at the corresponding temperatures of combustion are shown in columns 1 and 2 of Tables 7 to 14, inclusive, for the various carbonaceous materials, whose analyses are given in Table 6.

The most striking characteristic of the above expression lies in its unusual term, the cube root of the weight less unfamiliar if described as the weight of the sample per unit area of surface. This "substitution" function defines the concentration of the reactant indirectly, but avoids the insurmountable handicap of measuring the absolute area of the coke surface at any defined instant.

The apparent linear dependence of log. weight and time in coke combustibility graph construction cannot be dismissed without comment. In the performance of a combustibility test, the range of observed weight readings of an average burning sample extends from approximately the initial weight (as an example, say, 15 grams) to a point where 80% of that weight has been burned away (3.5 grams). The time taken to effect combustion of such a mass of coke varies with the experimental conditions of test, e.g., the coke itself, the temperature of combustion, etc. The exact location of a smooth curve with respect to the 24 observations of a combustibility test of this "average" coke depends upon the subjective judgment of the operator, and this licence has in the case of the logarithmic hypothesis obscured a real slight concavity of the log. weight/time curve for cokes burning under the present experimental conditions. The greatest irregularities occur at a time when the vitiating conditions associated with the loss of ash at the conclusion of an experiment are operative, and to this factor was attributed the curvature of the "straight" line. With no theoretical basis for the then existing data, the acceptance of

TABLE 6.

Proximate Analyses of Cokes and other Carbonaceous Materials used in Combustibility Tests.

	Coke D.	Coke E.	Coke F.	Coke G.	Coke H.	Coke K.	Coal Briquette J.	Graphite.
Moisture.	0.2	0.4	1.1	0.4	0.5	2.6	6.9	-
Volatile Matter less moisture.	1.3	0.2	1.7	1.1	1.5	3.0	5.7	-
Fixed Carbon.	96.7	86.1	84.8	88.7	89.3	87.8	82.7	99.8
Ash.	1.8	13.3	12.4	9.8	8.7	6.6	4.7	0.2

In the following Tables k is expressed as $(\text{grams})^{1/3}/\text{minute}$ and T in the absolute temperature scale. The calculation of k in the ignition range has not been attempted.

TABLE 7.

THE MORGAN CRUCIBLE CO., MANUFACTURED GRAPHITE.

For this material, the relation between k and T is given by the equation,

$$\log.k = -\frac{836}{T} + 1.0979.$$

k.	Temperature. °C.	log.k.	Calculated log.k.
2.203	930	0.3424	
2.670	975	0.4265	0.4281
3.050	1088	0.4843	0.4837
3.310	1173	0.5198	0.5198
3.550	1262	0.5502	0.5533
3.800	1360	0.5798	0.5860
4.250	1471	0.6284	0.6179

TABLE 8.

COAL BRIQUETTE J.

For this material, the relation between k and T is given by the equation,

$$\log.k = -\frac{568}{T} + 1.0302$$

k.	Temperature. °C.	log.k.	Calculated log.k.
3.111	765	0.4928	0.4830
3.430	858	0.5353	0.5380
3.692	942	0.5670	0.5628
3.905	1034	0.5911	0.5957
4.110	1105	0.6138	0.6253
4.283	1175	0.6314	0.6380
4.500	1240	0.6532	0.6548
4.670	1300	0.6693	0.6691
5.103	1425	0.7076	0.6957

TABLE 9.

COKE D.

For this material, the relation between k and T is given by the equation,

$$\log.k = -\frac{510}{T} + 0.9684$$

between the approximate limits of temperature, 830°C. 945°C.

Above 896°C, the relationship is given by,

$$\log.k = -\frac{954}{T} + 1.3490.$$

k.	Temperature. °C.	Log.k.	Calculated log.k.
2.333	775	0.3674	
3.175	830	0.5011	0.5061
3.640	930	0.5611	0.5445
4.037	1000	0.6053	0.5996
4.170	1042	0.6200	0.6236
4.533	1110	0.6561	0.6549
5.364	1222	0.7292	0.7193
5.650	1342	0.7520	0.7583
6.320	1485	0.8007	0.8064

TABLE 10.

COKE E.

For this material, the relation between k and T is given by the equation,

$$\log.k = -\frac{510}{T} + 0.8336$$

between the approximate limits of temperature, 800°C 1040°C.

Above 1040°C, the equation takes the form,

$$\log.k = -\frac{1500}{T} + 1.5880.$$

k.	Temperature. °C.	log.k.	Calculated log.k.
2.310	804	0.3636	0.3601
2.560	915	0.4082	0.4043
2.733	1022	0.4378	0.4398
2.860	1075	0.4771	0.4772
3.312	1128	0.5198	0.5178
3.590	1182	0.5551	0.5572
4.000	1250	0.6030	0.6037
4.530	1328	0.6561	0.6515
5.050	1430	0.7033	0.7076

TABLE 11.

COKE F.

For this material, the relation between k and T is given by the equation,

$$\log.k = -\frac{510}{T} + 0.8224$$

between the limits of temperature, approximately, $\begin{matrix}840^{o}C.\\1050^{o}C.\end{matrix}$

k.	Temperature. °C.	log.k.	Calculated log.k.
2.260	840	0.3541	0.3642
2.500	935	0.3979	0.4003
2.732	1040	0.4362	0.4340
3.360	1132	0.5263	

TABLE 12.

COKE G.

For this material, the relation between k and T is given by the equation,

$$\log.k = -\frac{510}{T} + 0.7614.$$

This condition holds between the limits of temperature, 835°C to 1200°C.

Above 1200°C, the relationship is given by,

$$\log.k = -\frac{3030}{T} + 2.3925.$$

k.	Temperature. °C.	log.k.	Calculated log.k.
1.803	820	0.2553	
1.963	835	0.2923	0.2998
2.070	863	0.3160	0.3135
2.162	930	0.3365	0.3375
2.333	1025	0.3674	0.3685
2.500	1128	0.3979	0.3974
2.800	1246	0.4472	
3.290	1338	0.5172	0.5117
4.000	1425	0.6020	0.6081
4.930	1510	0.6928	0.6929

TABLE 13.

COKE H.

For this material the relation between k and T is given by the equation,

$$\log.k = -\frac{510}{T} + 0.8565$$

between the approximate limits of temperature, $\begin{matrix}838^{o}C.\\1000^{o}C.\end{matrix}$

Above 1000°C, the equation becomes,

$$\log.k = -\frac{980}{T} + 1.2752.$$

k.	Temperature. °C.	log.k.	Calculated log.k.
1.744	770	0.2405	
2.500	855	0.3979	0.4044
2.760	952	0.4409	0.4402
2.900	1000	0.4624	0.4557
3.182	1025	0.5024	0.5202
3.571	1092	0.5527	0.5573
4.000	1175	0.6021	0.5991
4.480	1295	0.6513	0.6502
4.762	1365	0.6776	0.6770
5.080	1450	0.7059	0.7065

TABLE 14.

COKE K.

For this material, the relation between k and T is given by the equation,

$$\log.k = -\frac{510}{T} + 0.8744$$

between the approximate limits of temperature, $\begin{matrix}820^{o}C.\\975^{o}C.\end{matrix}$

Above 975°C, the relationship is given by,

$$\log.k = -\frac{2000}{T} + 2.0632.$$

k.	Temperature. °C.	log.k.	Calculated log.k.
2.163	775	0.3345	
2.571	825	0.4099	0.4100
2.833	935	0.4518	0.4521
3.480	1040	0.5416	0.5400
3.700	1080	0.5682	0.5846
4.920	1180	0.6920	0.6868
5.444	1242	0.7356	0.7431
6.730	1345	0.8280	0.8272

---

a linear dependence of log. weight and time can be understood.

The exceptions to the empirically formulated log. law magnify the inherent curvature of these curves by extending the range of observations of (a) weight and/or (b) time beyond the confined limits of the "average" grade of coke, and this is illustrated by the following examples.

(1). A complete combustibility curve for the dense manufactured graphite of these experiments entails 40 readings compared with 24 for "average" cokes. The appropriate curves are shown in Fig. 12.

(2). The effect of burning all cokes, etc., with reduced air supplies is to elongate the log. weight/ time curve in the direction of the time axis. This produces the bilinearity common to (1) and this is shown in curve of Fig. 14.

Under all experimental conditions, however, the mathematically deduced cube root law satisfies the results of any combustibility test rigidly. The one apparent exception, anthracite, can be correlated by a corollary to the fundamental assumption of the cube root equation, and this is fully treated below.

An investigation of the combustible properties of the "semicokes" (of which family the anthracites may be considered a natural member) was a logical step in the application of the present test, in whole or in modified part, to the problem of the burning of all solid fuels. The analyses of the anthracites used in these experiments are shown in Table 15 under columns A and B, together with the self-explanatory diagram of the geological conditions of Fig. 18. The effects of whin intrusion near the Knott seam are reflected in the differences in physical properties of the 2 types of anthracites. The burnt anthracite, for example, while retaining the banded structure of the original bedded material, is dull, powdery, columnar and easily ground, whereas the "normal" variety is lustrous, hard and splintery. These contrasting characteristics complicated the preparation of the standard test pieces from either material, since under pressure on the grindstone the samples cracked along incipient cleavage planes or flaked conchoidally. Drilling was impossible and this led to the introduction of a thin walled alundum

Fig. 18.

Diagrammatic sketch of Coalfield from which Anthracites were taken.

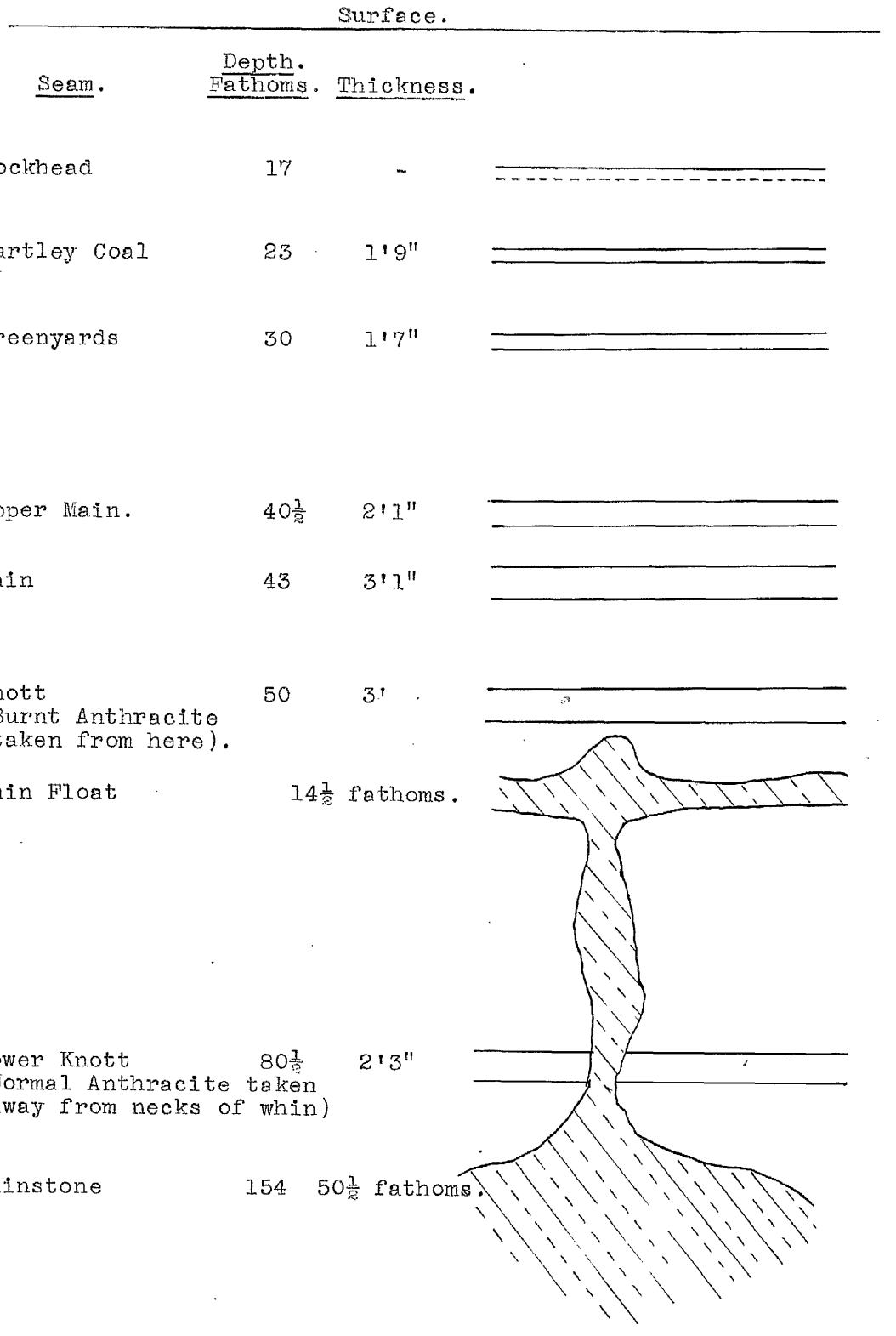

TABLE 15.

ANALYSES OF ANTHRACITES.

	Burnt Anthracite.	Normal Anthracite Average Sample.	Normal Anthracite Special Sample.
Moisture.	2.3	2.3	2.4
Volatile Matter less moisture.	6.9	7.9	7.7
Fixed Carbon.	84.7	87.2	87.7
Ash.	6.1	2.6	2.2
	A.	B.	C.

---

container as a modification of the usual suspension. The choice of design was determined by the preheating conditions of the test, since in attaining the combustion temperature the normal heat saturation of the specimen was accompanied by spalling and mechanical cracking, and the semi-solid side wall of the container prevents the collapse of the component fragments of the shattered anthracite. The contributory causes of this rupture are twofold.

(1). There is a large evolution of gas during the preheating time. The amount of this evolution can be gauged by the loss of 5.5 grams during preheating.

(2). The inherently brittle nature of the physical structure, which only weakly resists the high internal pressures developed by (1).

For the first series of experiments the samples were chosen indiscriminately from the block masses of the "normal" anthracite (as received), each sample providing two standard speciments to be used as duplicates. The combustibility test is completed under the standardised conditions of air rate and pressure, hitherto used, and the usual observations of weight and time made. This experimental technique is unsatisfactory, however, since it fails to control the conditions of the experiment and, consequently, makes the duplication of results impossible. This lack of control is due primarily to the shattering of the anthracite, which is subject only to the statistical laws of chance, and in a lesser degree to the unknown distribution and structural arrangement of the petrological constituents. That the fragmentation of the anthracite cannot be accurately estimated is shown by the following "counting" experiment. Two matched samples were lowered at the same rate into a furnace at 900°C, and left for 5 minutes. When withdrawn, one had split into 8 and the other into 12 parts.

For various reasons, graphical presentation of the results obtained does not readily reveal the effect of the complicating variables mentioned above, and the method of Table 16 has, therefore, been adopted for reference in the following explanatory statement. All deductions from these results, however, are

TABLE 16.

Showing the effect of the complicating variables, affecting the combustion of anthracite.

	Condition of sample.	Temperature of experiment. °C.	Weight lost by Combustion of Standard Sample.	Time taken to effect stated loss. m.	s.
A.	With laminations parallel to air blast.	822°C.	8.0 grams.	30	05
	With laminations transverse to air blast.	822°C.	8.0 grams.	34	05
	Laminations transverse to air blast for all further experiments.				
B.	Showing the effect of uncontrolled rupture of the specimen.	(1) 1200°C	9.5 grams.	25	23
		(2) 1270°C	9.5 grams.	28	07
C.	Crucible with crack along its length.	1120°C.	9.0 grams.	20	34
	Crucible without crack along its length.	1120°C.	9.0 grams.	25	35
D.	Samples taken indiscriminately from the general sample.	(1) 972°C.	8.0 grams.	22	12
		(2) 990°C.	8.0 grams.	35	52
E.	Showing that circumstances may operate to allow of duplication.	(1) 1035°C.	9.5 grams.	36	57
		(2) 1045°C.	9.5 grams.	36	51

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contingent on a recognition of the assumption that in the duplication of experiments with samples taken from the same block, the variability of the shattering does not entirely obliterate the effect, named as responsible for the difference in combustibility.

By increasing the surface area accessible to the air blast, the rate of combustion is naturally accelerated (25,26). The origin of the areal extension is the lamellar junctions of the banded anthracite which, as planes of mechanical weakness, are prone to incipient cracking. Condition A of Table 16 would appear to show that the rate of reaction depends upon the relative direction of the exposed surface area to the air stream, but since this conflicts with the proved statement that "the original volumetric outline is preserved throughout combustion", the conclusion must be accepted with reserve. Nevertheless, as a precautionary measure, to eliminate this "variable" in all further experiments the anthracite samples are ground to have the bands horizontal, i.e., transverse to the direction of the air stream.

Condition B proves indirectly the assertion in the first sentence of the last paragraph. By the uncontrolled rupture of the specimens, a coal can appear to burn quicker at 1200°C than at 1270°C, showing that the degree of shattering may neutralise and, as in this case, even reverse the effect of increased temperature on combustibility. The sensitivity of the anthracite to variations in the air supply (26) is illustrated by Condition C. During a duplicate experiment, the alundum container developed a crack in its side wall, which afforded the air blast an alternative and easier route to the combustible surfaces. The increased combustibility is a measure of the increased concentration of the gaseous reactant. The intentionally indiscriminate sampling of Condition D illustrates the effect of petrological differences, whereas example E is an isolated instance of the possibility of duplicating results. The chances by these experiments of duplication are 1 in 40.

The difficulties of proper sampling are apparent but are eliminated by confining the second series of experiments to standard specimens taken from a slab, 1 1/8 ins. thick. The analysis of this special sample is given in Table 15 under that heading, and a graphical record of the changes in combustibility with temperature in Fig. 19. The choice of ordinate (W-b) for the construction of this Figure, though arbitrary, forms a convenient and derived mathematical mode of expressing the further circumstances of the burning of anthracite.

The fundamental theory of combustion stresses the vital part played by the surface area of the material exposed to the air, but equally essential to the theory is the progressive diminution of the original surface outline during burning. By enlarging the scope of the underlined term to include the total surface area of all the fragmented portions of the mechanically ruptured anthracite prior to the start of combustion, it is possible to account mathematically for the progress of anthracite combustion. There are two possibilities.

(1). That combustion proceeds from the surface of the defined areas in such a way that the various and irregular shapes of the original parts of the cylindrical whole are preserved in miniature. This condition is comparable to that used to express the mechanism of coke combustion, and as previously,

$$(W-b)^{1/3} = -kt + C.$$

(2). That concurrently with the above action there is a further shattering of the brittle anthracite, the effect of which is to expose a greater area to the blast than would normally be exposed at the same instant by continued combustion under the conditions of (1). The extent of this secondary breakage is not accurately known for any temperature but the rate at which fresh surfaces are formed may be

(a) less than,
(b) equal to, or
(c) greater than

the rate at which the total surface area is being reduced by combustion. Some uncertainty surrounds the mathematical expression of conditions (a) and (c) but for (b),

$$-\frac{dW}{dt} = k'$$

$$\text{or,} \quad (W-b) = -k't + C'. \qquad (23).$$

This simplified formula has been used as a datum line to determine which of the three possibilities detailed above is the appropriate for the specific experimental temperature under consideration.

The curves for experiments at 815°C and 880°C, which are

Fig. 19.

The effect on Combustion of Secondary Rupture of Anthracite.

Note - Rate of air supply for these experiments is 59.9 gms./min

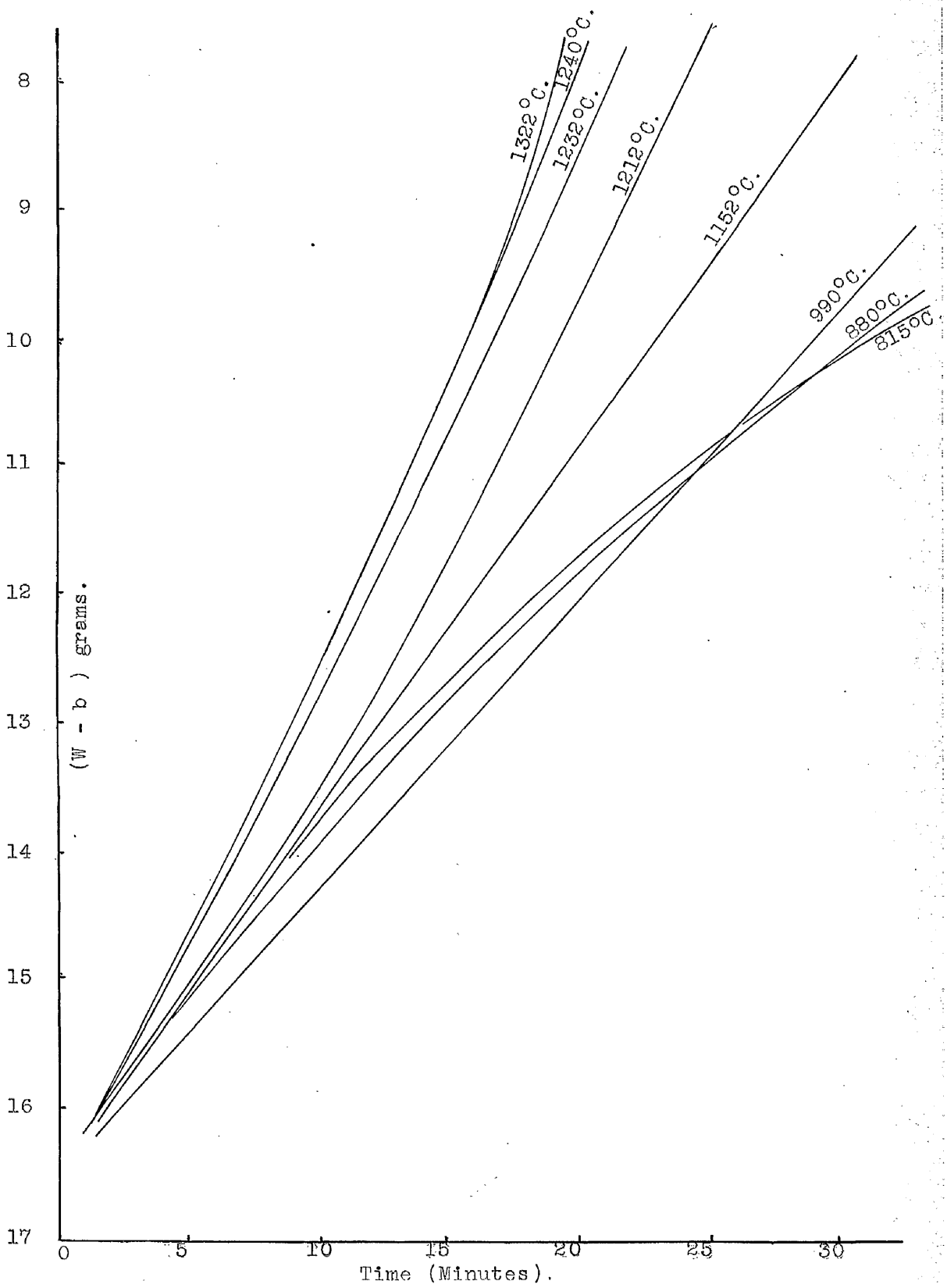

Figure on curve denotes temperature of Combustion.

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concave to the time axis in Fig. 19 are linear when redrawn to a scale of $(W-b)^{1/3}$/time. This confirms an impression gained in the first series of experiments, that at the low combustion temperatures either of the conditions (1) or (2a) holds, i.e., either primary rupture is completed during the preheating time to these temperatures, or alternatively the amount of secondary carcking during combustion is slight. From 1000°C to 1150°C, the secondary rupturing following on the normal primary cracking approximates to a stage, where condition (2b) is effective, i.e., as much fresh surface is formed by rupture as is removed by combustion. Above 1150°C, there is an acceleration of the final phases of combustion, witness the convexity of the curves to the time axis, implying a rapid rate of areal increase due to shattering. It must be recognised that these curves give no idea of the extent of primary rupture during preheating, and this can only be measured by the "counting" method. The combustion at surfaces other than that of the superficial area of the cylindrical sample is very well shown by the presence of internal bands or layers of ash. The composition of the inherent ash is variable, illustrated by the different coloured bands which separate one constituent of the anthracite from the adjacent one, but surprisingly no distinctions in colouring are noticeable in the usual ash layer surrounding the sample as a whole.

The third and final series of experiments with the anthracitic coals was made with the burnt variety, the analysis of which will be found in Table 15. The combustibility test conditions are the same for the present series as for the previous ones. By slowly lowering the standard specimen into the furnace, however, it was found possible to reduce to a minimum, if not entirely prevent, the shattering so characteristic of the ordinary anthracite. A small amount of interleaving of the coal with layers of ash is visible at the end of experiments - probable evidence of a slight internal cracking. The usual observations of weight and time are taken and plotted to a scale

Fig. 20.

Normal Combustibility Curves for Anthracite in the absence of secondary rupture.

Note - Rate of air supply for these experiments is 59.9 gms./min.

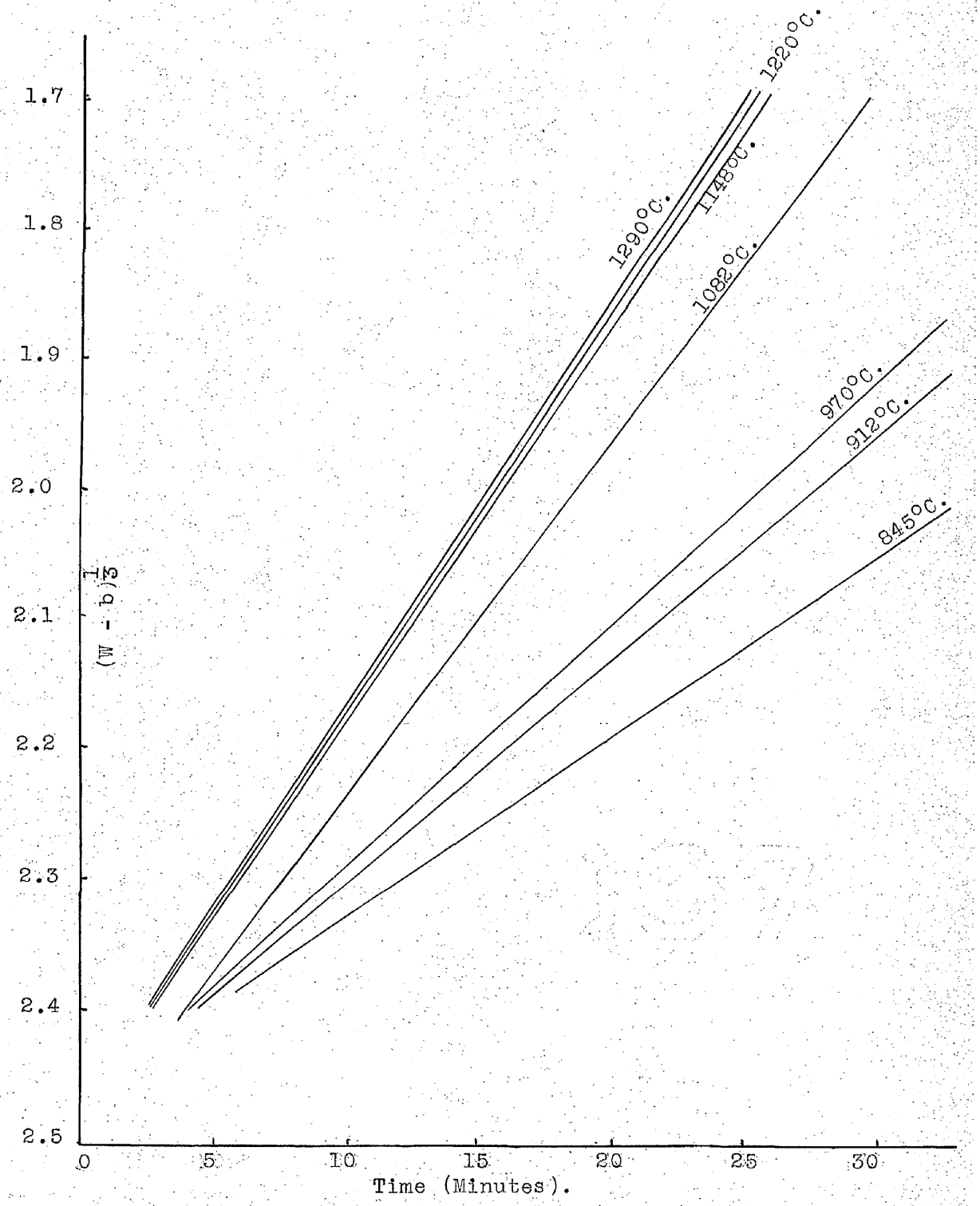


Figure on Curve denotes temperature of Combustion.

of $(W-b)^{1/3}$/time, as shown in Fig. 20. The linearity of these curves in the range of temperature quoted is in complete contrast to the variable curvatures of the curves of Fig. 19. As to whether this can be considered a true satisfaction of the general theory of combustion, or whether condition (2a) may also be operative to some small degree, some doubt must remain. The general application of the same formula, however, allows of the comparative measurement of the curve gradient for each temperature and the construction of a combustibility/temperature curve on a thermodynamical basis to be discussed later.

The position may, therefore, be summed up thus. That for all solid fuels, which do not disintegrate during combustion, the condition $\frac{d(W-b)^{1/3}}{dt}$ remains constant for any temperature. If corresponding values of $(W-b)^{1/3}$ and time are plotted graphically, the above constant is measured by the tangent of the acute positive angle between the time axis and the curve itself. The particular value of the constant for any fuel variety increases with temperature, but the formulation of a probable relationship between these functions is postponed for a survey of the physical characteristics of combustion.

At the end of every combustibility experiment, the sample is examined macroscopically. As removed from the furnace, the test piece consists of a core of unburnt coke, a replica in contour and dimensions within near limits of the original geometrical shape and proportions. This core is surrounded by an ash covering whose external surface is similar to the configurations of the initial coke standard, but above the melting point this ash "coat" is dispersed indiscriminately on the coke surface as molten globules. The reproduction in miniature of the coke at any stage of the combustion is independent of the surface incombustible, and this cannot be overstressed since it emphasises the distinction between the logarithmic and cube root theories of burning. The choice of the latter is not merely an academic question of exactitude as against approximation, but a distinction in the deeper and more fundamental physical

interpretation of the mechanics of combustion.

The empiricism of the log. theory and the thickening of the ash cover as combustion proceeds led to a tacit assumption that the determining condition of combustion was the rate of diffusion of air through the ash cover, which when solid acted as an increasingly resistant semi-permeable barrier to the penetration of the air stream to the underlying carbonaceous surface. No explanation was tendered for the persistence of the diminishing rate of weight loss when the ash melted, since by the globularisation of the ash on liquefaction fresh coke surfaces were exposed with no impediment to the air blast. By the assumptions of the cube root law, however, the ash in whatever form or content it may be present is relegated to secondary importance as the neutral filling matter, and can be dismissed as the mechanically controlling factor of combustion. The outstanding condition which regulates the rate of combustion is the extension of the combustible surface area, the role of the ash being that defined above. To this limitation of ash function must be added the proviso that all ash compositions have so far been of low interfacial tension, and do not wet the surface of the coke. The effect of a thin liquid film over the burning surface would naturally introduce a new vital factor.

A distinction must be made at this stage between the ash which appears as thin flat shaly pieces, brown or white in colour, and the ash which exhibits the cellular structure of the coke. It is the latter with which this discussion is concerned. The appearance and coherent strength of the ashes of the cokes of this work vary because of the differences in both composition and distribution. For example, the ash cover for Coke G is more coherent than that of Coke E, and this may be due to the larger pores of the latter which burn to a "strained" or weakly supported cell wall. The percentage ash also affects this strength and the thickness of the cell wall of ash may assume molecular proportions or large thicknesses either leading to ultimate collapse. An analogy to ash behaviour would be the relative

strengths of different sizes of soap bubbles with varying thicknesses of soap film. The comparatively low ash of the briquetted coal coupled with its structureless character produce a furry deposit, which below its melting point sinters to give the effect of a peeling skin. A somewhat similar effect is seen in the experiments with the anthracite of the second series of experiments.

Visual examination of the transverse and longitudinal sections of the core reveals a narrow metallic grey rim, 1.0 mm. in depth, surrounding a still inner core. This rim is apparently a shallow zone of renewed coking at a temperature higher than that experienced in its previous industrial manufacture, and a minimum estimate of this skin temperature in the initial stages of the combustibility test as distinct from the recorded wall temperature is shown in Table 17. The first few points of the cube root curve lie on a curve of steeper gradient than the later readings due to the transient conditions operative at the commencement of the test. By calculation of this gradient of intense combustion and the temperature corresponding to it, column 3 of Table 17 has been compiled. The observed temperatures of column 2 have been obtained with a Vanner optical pyrometer and are not truly comparable to those of column 3, since the calculated figure refers to the shallow layer at the surface of the coke, whereas the observed figure measures the average rise over the whole top surface of the coke. This probably accounts for the discrepancy in the two columns.

In contrast to the invariability of the appearance of this rim is the changing aspect of the inner core. This may under certain experimental conditions be indistinguishable from the original coke, sooty or even oily but generally, since infrequent exceptions have been noted, the nature and extent of core changes depend upon the previous history of the coke in relation to the temperature and time of its combustion. This "historical" condition determines the range of temperature below which no positive visual change in the core is effected. Interruption

TABLE 17.

Rise in surface temperature of coke associated with the passage of air blast.

	Temperature of coke before the passage of air blast. (°C).	Observed temp. rise in coke after passage of air blast. (°C).	Calculated temp. rise in coke after passage of air blast. (°C).
COKE E.	890	90	275
	1000	60	228
	1125	45	125
COKE D.	890	65	160
	1018	65	110
	1130	0	0

of the combustibility tests at irregular time intervals have shown that within certain limits of observation the extent of core modification is a function of the time interval that the coke is above the critical temperature range. These factors evidence decomposition of the coke as the obvious explanation, the instability attaining noticeable proportions at and above the range of temperature of coking manufacture of the specimen under test. This statement agrees with the definition of temperature of "recarbonisation" given in Chapter 1 and will be more accurately defined in the discussion of the curves of combustibility/temperature to follow.

A feature of the modern attitude to homogeneous chemical reactions has been the thermodynamical bias attaching to the elucidation of the problems of such reactions based upon the Arrhenius equation (27),

$$\frac{d(\log.k)}{dT} = - \frac{E}{RT^2} \qquad \text{----------(1),}$$

representing the variation of the reaction velocity k with temperature T. R is the well known gas constant. Various interpretations of the constant E the "energy of activation" have been mooted, but for the present the author feels justified in defining E as the minimum energy which the molecules of the two reacting substances between them must possess in certain form or forms before chemical reaction can be initiated and maintained. The difficulties associated with heterogeneous reactions, however, are manifest and it is proposed without proof to use an analogous concept to equation (1) to correlate the observed rates of reaction of heterogeneous activity with temperature, i.e.,

$$\frac{d(\log.k)}{dT} = - \frac{A}{RT^2} \qquad \text{----------(2).}$$

k and T are interpreted as in eqn. (1). A is proportional to the energy requirement for the combustible/air reaction. Integrating the above equation

$$\log._e k = - \frac{A}{T} + B \Big)_{T_1}^{T_2} \qquad \text{-----(3).}$$

B is the integration constant.

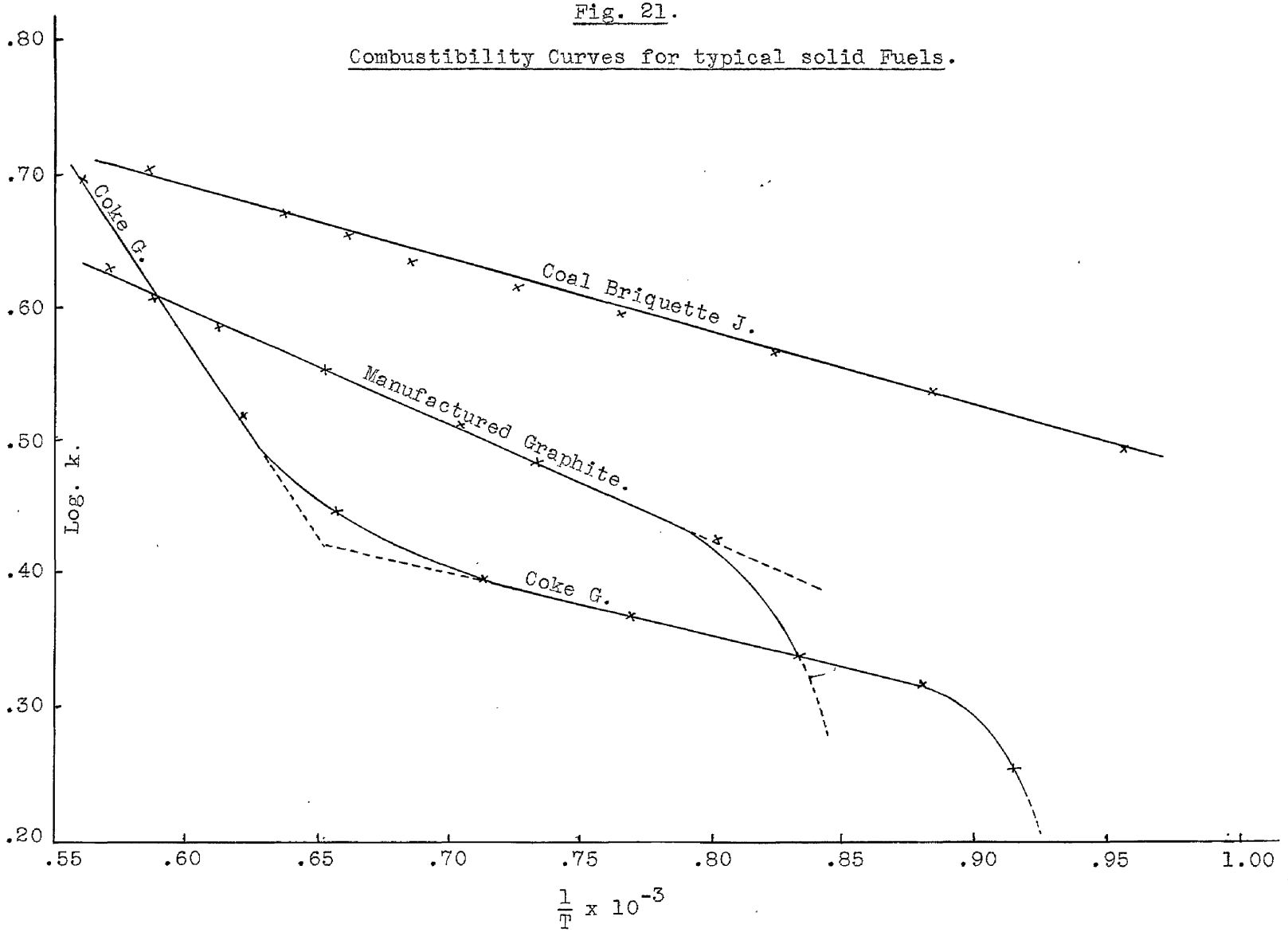
The definite integral limits are imposed since the linear expression can only be taken to apply within a range of temperature, T_{12}, where the mechanical processes of combustion are comparable and the only variable is temperature. The method adopted for the presentation of the facts on this hypothesis is that of Tables 7 to 14. Columns 1 and 2 detail the observed values of k and the temperature of its measurement. The equations satisfying these results are given in the prefaced remarks to these Tables, and the difference between the observed values of log. k and the values calculated by these equations can be compared by columns 4 and 5. Fig. 21 reproduces graphically the corresponding values of log.k (the base of eqn. (3) is changed from the Napierian to the common logarithm) and $\frac{1}{T}$ of Tables 7, 8, 12 for the "artificial" materials, graphite and coal briquette for Coke G. The curves for these materials have been chosen as representing all the possible curve types obtained by the application of equation 2.

The linearity within certain temperature limits of the curves for the pressure formed briquette and graphite would appear to serve as prima facie evidence of the proposed theoretical assumptions embodied in the equation. Below the lower limit T_1 of eqn. (2) and within a narrow range of this temperature, the straight line tends to develop a curvature such that the rate of reaction falls rapidly to zero, and this deterioration in combustibility is due to the chilling effect of the air blast on the coke surface layers, which are cooled to a temperature at which continued combustion becomes impossible. While the experimental technique does not allow of the accurate measurement of the rate of reaction within this range at close temperature intervals, the upper limit T_1 of the "ignition range" of a coke is advanced with an increase in the rate of air supply and the density equivalent. This latter term is the mass of the standard sample used in these experiments.

There is no reason to suppose that the curvature of the ignition range is discontinuous with respect to the assumed

Fig. 21.

Combustibility Curves for typical solid Fuels.



combustibility/temperature equation. Consider the alternative expression to the logarithmic form of eqn. (3).

$$k = Ce^{-\frac{d}{T}\Big)_{T_1}^{T_2}} \qquad \text{----------(4),}$$

where C = antilog$_{10}$ B. This exponential form, though applicable to the major portion of the graphs of Fig. 21, may be only one term of a general expression. By delimiting the temperature range for which the Arrhenius conception is valid for the same reactants (i.e., excluding allotropic and other changes) the variation of combustibility with temperature from ignition can be expressed by

$$k = Ce^{-\frac{d}{T}} + Fe^{-\frac{g}{T}} \qquad \text{----------(5).}$$

The values of the constants F (which may be negative) and g are such that above the ignition range the arithmetical value of k is not significantly affected by the second term of eqn. (5). With the present insufficiency of data, the author in Tables 7 to 14 has restricted the temperature limits to those of stabilised combustion and excluded any mathematical consideration of the conditions of the ignition range (28).

The hybrid curve for the typical coke is a comparable repetition of the curve for graphite from ignition to an upper finite limit, which varies for the particular grade of coke. Above this temperature limit the curve continues to the highest temperature as another straight line of steeper gradient. No one simple equation will perhaps satisfy all the observed rates of reaction for any one coke, but the true import of the extension of the linear relationship lies in the continuity of the mechanics of combustion throughout the whole range of temperatures, in the recognition that the difference in the upper range of temperature is a difference of degree, not kind, and that that difference is to be measured by a change of constants and not by a change in the fundamental equation. The composition and particle size of the coal charge to the oven, the carbonising conditions, etc. (29), all determine the particular

temperature at which the discontinuity shows, but since industrial practice does not confine these variables to precise limits even in the same oven, the change in some cases occupies a range of temperature. The quotation of a specific temperature is convenient, however, and is calculated by the extrapolation of the two straight lines at their junction.

The identification of the conditions determining the transition temperature of coke behaviour with the conditions of recarbonisation (see Chapter 1) emphasises the distinction to be made between the "stable" and "metastable" phases of coke, the transition boundary being determined by the complete history of manufacture previous to combustion. The term "coke" is indefinite in that it is applied to all products of a thermal process of infinite variability, thereby obscuring the fact that any one coke is not an ultimate entity but a product stable within the temperature limits of its production, though subject to further transformation when these limits are transcended. Where, for example, the maximum temperature of combustibility does not approach the formation temperature of graphite ($2000^{o}C$) or where the burning material undergoes the same processes of change throughout the temperature range of combustibility as for the coal briquette, for these materials there is no hybrid combustibility curve but the straight lines of Fig.21 since there is no change in the mechanism of combustion within the range of these tests.

In formulating a theory to account for the effect of temperature on reaction velocity, the author has rejected any mechanistic explanation in the present state of knowledge of the complications of atomic surface structures of coke at room and (more important) combustion temperatures (13). Experience of other heterogeneous reactions has shown the value of the energy concept of Arrhenius, and the assumption of its modification here avoids the speculation of possible atomic and molecular activity. By extending the analogy further, A is defined as a function proportional to the minimum energy which the molecules

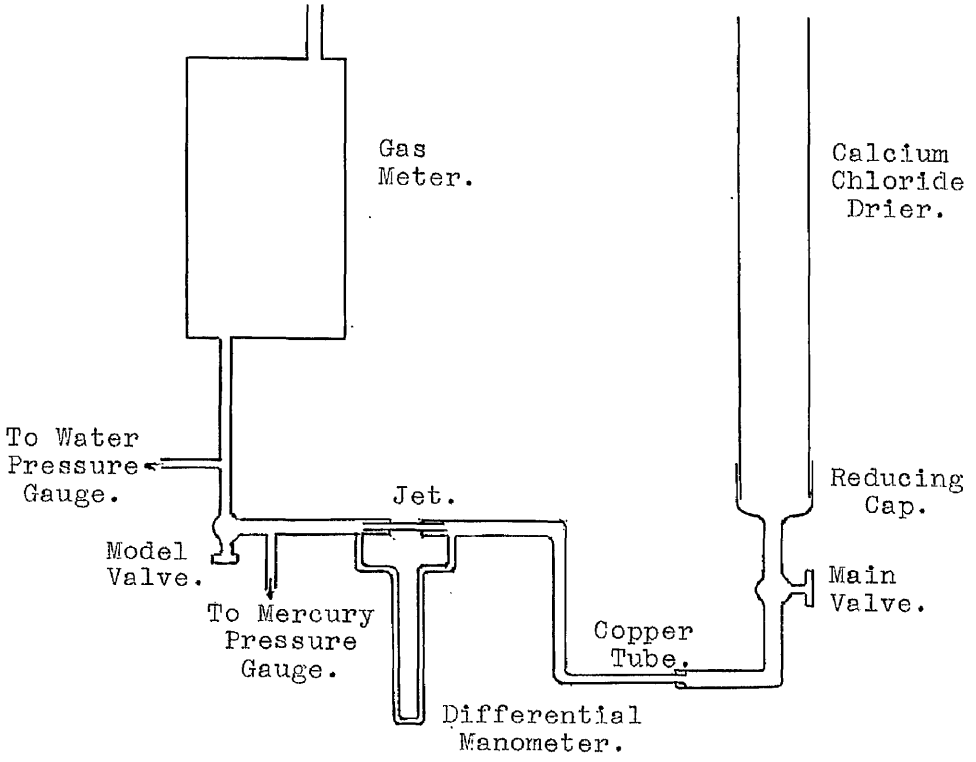
of the reactants of the coke/air reaction between them must possess in certain form or forms for the maintenance of combustion. Any particular minimum value is operative only within the temperature limits of similar internal activity (if any) of the fuel, whether due to recarbonisation or graphitisation, but the dependence of combustibility on temperature is unaffected by the degree of activity.

With the air supply of these experiments, the value of A is peculiar to the individual materials listed in Table 6 and 15 for the burnt anthracite. The arithmetical values of the constants A and B of eqn. 3 for these fuels are essentially arbitrary functions of the system of units adopted. In addition, however, both constants are the end products of the summation of a series of terms mathematically defining the effect of the variables affecting combustibility. These factors include the catalytic activity of the surface, the volatile matter and ash of the fuel. the density equivalent and shape of the burning solid and the rate, pressure and moisture of the air supply, but the measurement and proper apportionment of these factors in the final figure A or B remains unsolved. Lacking mathematical coordination of these variables for calculating A, for all cokes in the lower range of temperature A has been reported as the constant -510. This simplification has no theoretical basis in fact, but since the number of points which can be observed within this short range of 150^{o}C is limited by the experimental technique, the above gradient has been chosen as a near approximation to the real value of the gradient. As will be shown later, this arbitrary constancy of A for all cokes is not duplicated for other lower rates of air blast.

The omission of any reference in the definition of A to the initiation of combustion is intentional (cf. E in eqn. 1), and is a consequence of the discrepancy between experimental results in the ignition range and those calculated by eqn. 3. The second term of the extended Arrhenius equation, eqn. 5, introduced to correct this existing difference is a measure of

Fig. 22.

Layout of Apparatus for Calibration of Jet for measurement of Air Flow.



the complex activity of oxygen at a carbon surface (investigated in Chapter 1) at or preceding ignition, a measure of the inertia of the carbon to burn. The negligible value of this term above the ignition range has already been noted. It is doubtful whether this denotes a virtual disappearance of the precedent consecutive reactions to combustion or an intense acceleration of these reactions.

The calculation of B from the constants of the fuel, i.e., ash, density equivalent, etc., has been unsuccessful also. An attempted correlation of B with the calorific value of the fuel has shown some dependence but no definite relationship has been established. There appears to be no definition of B comparable to that of A from the Arrhenius equation analogy.

No precise argument has been adduced to justify the adoption of the Arrhenius equation to relate the reaction velocity of the coke/air reaction with temperature, and other possible empirical equations exist. Only consideration of combustion as an ordinary heterogeneous chemical reaction obeying the laws shown theoretically and practically to exist for similar types of reactivity, can justify the assumption of these same laws for this case. Until further evidence accumulates to prove that combustion is an exceptional chemical activity of Nature, there can be still less reason for an empirical formula to replace that assumed in this discussion.

The research so far reported has been confined to the effect on combustibility of only one experimental variable -- temperature. Two series of experiments were designed, therefore, to illustrate the changes in combustibility of -

(a). variations of the rate at which air is supplied to the coke sample (25,30), and

(b). alterations in the linear dimensions and contour of the standard coke test specimen (31).

The proper determination of (a) requires an exact knowledge of the value of the air rate and this is achieved by calibration of the Venturi meter in the air circuit with the design of apparatus of Fig. 22. (Cf. air circuit for combustibility test,

Fig. 23.

Combustibility Curves for Coke D, obtained using various rates of Air Supply for Combustion.

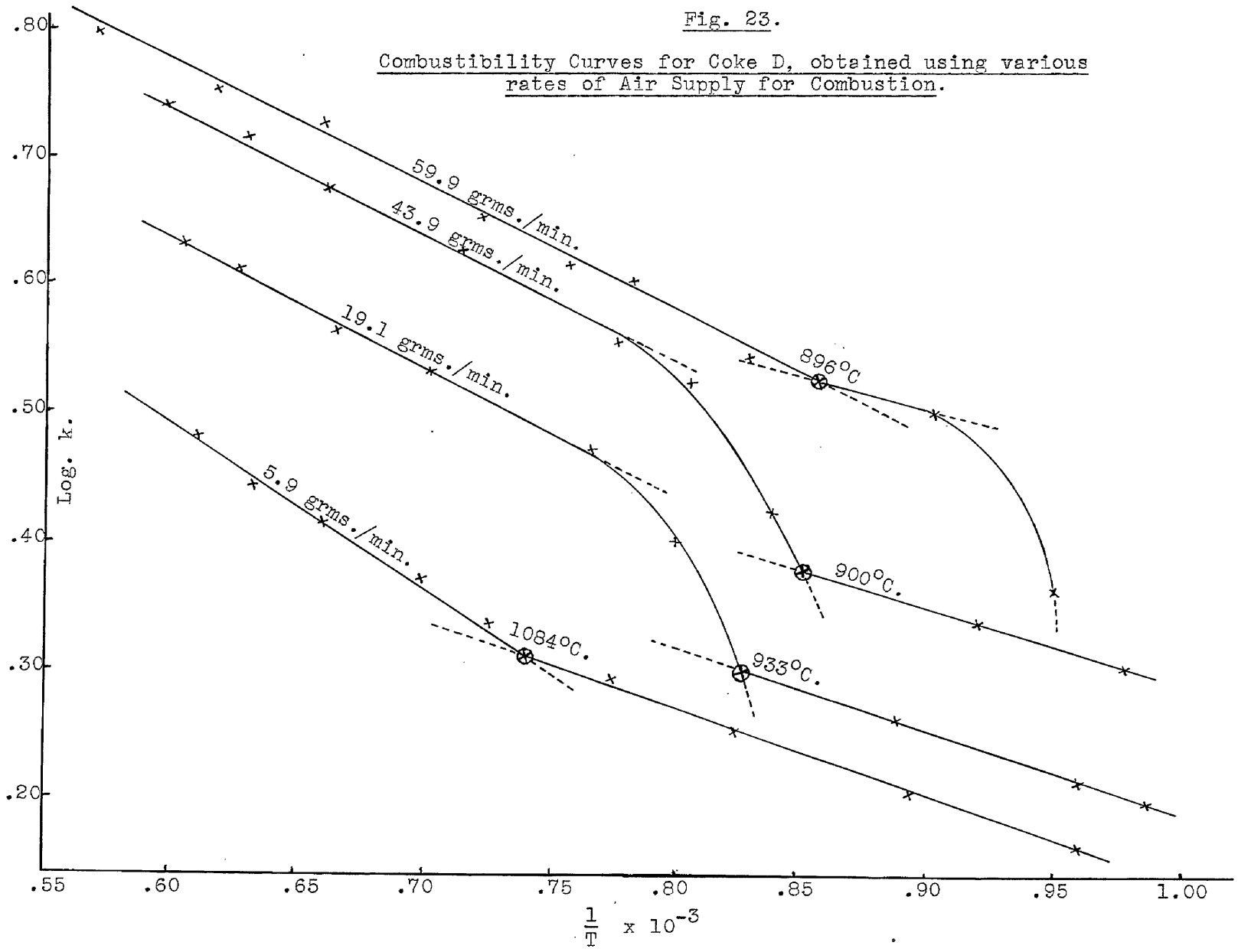


Fig. 24.

Combustibility Curves for Coke E obtained using various rates of Air Supply for Combustion.

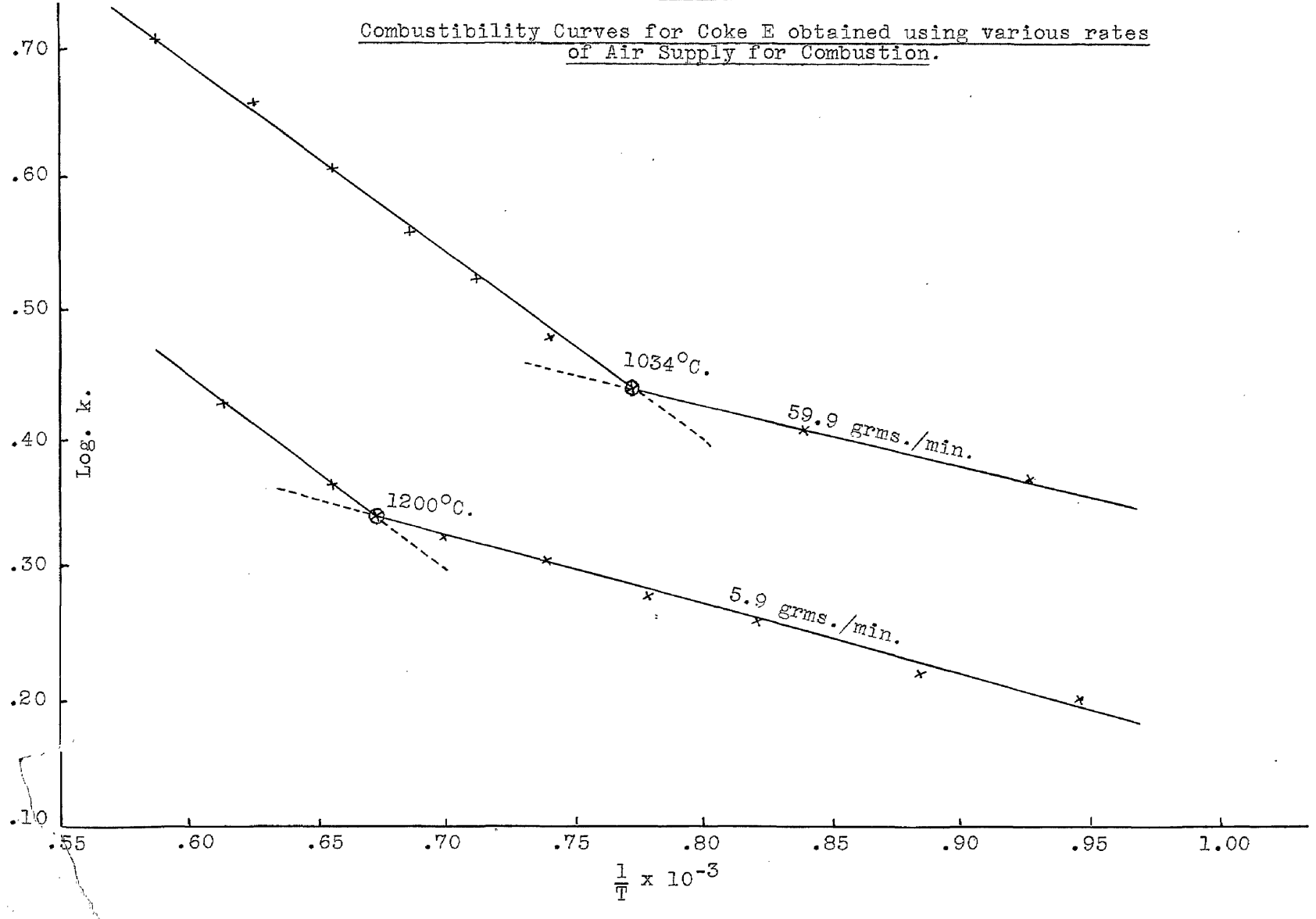


Fig.10). The meter is one corrected for error between the maximum and minimum rates of this series of experiments by the appropriate department of the Board of Trade. The range of air rates is controlled by adjustments of the main and model valves and for several of these rates the times taken to pass 10 and 20 cb. ft., the barometric pressure and the temperature of the air at the inlet to the meter are noted. With the allowance for the accuracy of the meter and with a knowledge of the density (gms./litre) under the experimental conditions of temperature and pressure, the air rate is calculated conveniently as grams per minute. This method of quotation of rates dispenses with the recital of the air conditions, temperature and pressure. Since the bore of the constricting jet of the differential manometer limits the range of rates which can be accurately measured, three different jets have been calibrated and used to give maximum readings of pressure for combustibility tests.

The usual combustibility test was performed with Coke D and Coke E with four and two different rates of air supply, respectively, and the complete data relating to these experiments are tabulated in Tables 18 to 21. The graphical representation of these results is given in Figs. 23 and 24 on the assumption of the validity of eqn. 3. In general outline, these hybrid curves are similar to those illustrating the combustibility/temperature behaviour of all cokes burned under the air conditions of the previous research. There are, however, certain differences which have been condensed for reference in Tables 22 and 23 for both cokes. With decrease in the rate of the air stream, there is -

(1). an increase in the value of A in both ranges of the bilinear curve,

(2). a decrease in the value of B in the lower temperature range,

(3). an increase in the transition temperature, and

(4). a decrease in the temperature at which ignition first becomes noticeable. This is not apparent in the curves themselves but is noticeable in practice.

TABLE 18.

COKE D.

Rate of air supply = 43.9 gms./min.

For this material, burning under the conditions of air supply detailed above, the relation between k and T is given by the equation,

$$\log.k = -\frac{566}{T} + .8630$$

between the limits of temperature, approximately, $\begin{matrix}745^{o}C.\\900^{o}C.\end{matrix}$

Above 900°C. the relationship is given by,

$$\log.k = -\frac{954}{T} + 1.3085.$$

k.	Temperature. °C.	log.k.	Calculated log.k.
2.030	745	0.3075	0.3074
2.195	812	0.3404	0.3414
2.670	918	0.4265	
3.360	966	0.5263	0.5386
3.630	1012	0.5599	0.5661
4.270	1125	0.6304	0.6261
4.761	1240	0.6776	0.6780
5.230	1312	0.7185	0.7066
5.524	1400	0.7419	0.7383

TABLE 19.

COKE D.

Rate of Air Supply = 19.1 gms./min.

For this material, burning under the conditions of air supply detailed above, the relation between k and T is given by the equation,

$$\log.k = -\frac{600}{T} + 0.7962,$$

between the limits of temperature. $\begin{matrix}735^{o}C.\\933^{o}C.\end{matrix}$

Above 933°C, the relationship between the two functions k and T_A is given by,

$$\log.k = -\frac{954}{T} + 1.2070.$$

k.	Temperature. °C.	log.k.	Calculated log.k.
1.590	735	0.2014	0.2010
1.653	763	0.2175	0.2171
1.822	850	0.2601	0.2620
2.000	930	0.3010	0.2975
2.531	975	0.4031	
2.994	1027	0.4757	0.4755
3.240	1088	0.5105	0.5056
3.390	1148	0.5302	0.5297
3.704	1230	0.5682	0.5723
4.083	1322	0.6117	0.6190
4.290	1380	0.6325	0.6299

TABLE 20.

COKE D.

Rate of air supply = 5.9 gms./min.

For this material, burning under the conditions of air supply detailed above, the relation between k and T is given by the equation,

$$\log.k = -\frac{660}{T} + 0.8022,$$

between the limits of temperature, approximately, $\begin{matrix}763^{\circ}C.\\1090^{\circ}C.\end{matrix}$

Above 1090°C, the relationship between the two functions k and T_A is given by,

$$\log.k = -\frac{1254}{T} + 1.2460.$$

k.	Temperature. °C.	log.k.	Calculated. log.k.
1.470	763	0.1673	0.1632
1.621	844	0.2095	0.2133
1.790	937	0.2529	0.2568
1.970	1015	0.2945	0.2898
2.180	1102	0.3385	0.3340
2.350	1155	0.3711	0.3749
2.604	1242	0.4150	0.4183
2.811	1305	0.4487	0.4514
3.050	1360	0.4843	0.4781

TABLE 21.

COKE E.

Rate of air supply = 5.9 gms./min.

For this material, the relation between k and T is given by the equation,

$$\log.k = -\frac{540}{T} + 0.7017$$

between the approximate limits of temperature, $\begin{matrix}782^{\circ}C.\\1200^{\circ}C.\end{matrix}$

Above 1200°C, the equation takes the form,

$$\log.k = -\frac{1666}{T} + 1.4621.$$

k.	Temperature. °C.	log.k.	Calculated log.k.
1.571	782	0.1959	0.1899
1.640	843	0.2148	0.2179
1.814	945	0.2577	0.2584
1.900	1012	0.2788	0.2755
2.000	1080	0.3010	0.3026
2.110	1168	0.3243	0.3270
2.333	1250	0.3674	0.3682
2.650	1330	0.4232	0.4228

TABLE 22.

Showing the effect of various rates of air supply on the constants A and B in both ranges of the combustibility curve for Coke D, and with the rise in temperature of the break with lower air blast.

Rate of air supply. (gms. min.)	A. Range below break	A. Range above break	B. Range below break	B. Range above break	Rise in Temperature. °C.
59.9	- 510	- 954	0.9684	1.3490	896
43.9	- 566	- 954	0.8630	1.3085	900
19.1	- 600	- 954	0.7962	1.2070	933
5.9	- 660	- 1254	0.8002	1.2460	1084

TABLE 23.

Showing the same effect as Table 22 above, but with Coke E in place of Coke D.

Rate of air supply. (gms. min.)	A. Range below break	A. Range above break	B. Range below break	B. Range above break	Rise in Temperature. °C.
59.9	- 510	- 1500	0.8336	1.5880	1034
5.9	- 540	- 1666	0.7017	1.4621	1200

The dependence of A (and of B) on the rate of air supply is especially significant. It defines the essential role of air in combustion by emphasising that the minimum energy for the continuance of combustion is not the contribution of one of the reactants but of both. (This condition had already been presumed in discussing the calculation of A from the fundamental constants of the reactants). Further, the differential of A with respect to the rate of air supply is a function of the fuel characteristics,and the assumption of a constant gradient for the temperature range above ignition for all cokes burning under the maximum rate of air supply of these experiments has, therefore, no factual evidence to support it. Its mathematical convenience is obvious.

The rise in the transition temperature exemplifies that tendency of all cokes to an ultimate stability, probably complete graphitisation, and the mergence of the hybrid curve to the single linear combustibility/temperature curve of graphite. Industrial coking, as the phenomenon of recarbonisation showed, is an interrupted stage in the attainment of this stability, a stage which can be advanced by further annealing at a higher temperature. The transition temperature defines the start of a "metastable" region of pronounced internal activity, but does not deny other possible internal activity below this temperature. The extension of the so-called "stable" range by decrease of the rate of air supply is an extension of the region of lesser activity, simulating true stability within the limits of experimental error of the test for combustibility. The rate of rise of the transition temperature with the lowering of the air supply rate differs for the two cokes and is more pronounced at the lower rates of air blast than at the higher. The peculiar breaks of the two middle curves of Fig. 23 have not as yet been explained, but it appears probable that lack of uniformity of the coke and improper sampling are responsible.

The depression of the ignition temperature with a reduction of the rate of air supply is to be inferred from the curves of

TABLE 24.

Showing the effect of shape and dimensions of the standard samples on combustibility.

(a) GRAPHITE.

Shape.	Dimensions. cms.	Ratio. Calculated Area / Weight of sample.	Combustibility k measured at 965°C.	Combustibility k measured at 1154°C.
Cylinder	Length - 2.38 Diameter - 2.06	1.45	2.600	3.260
Cylinder	Length - 2.85 Diameter - 2.54	1.24	2.588	3.236

(b) COKE D.

Shape.	Dimensions. cms.	Ratio. Calculated Area / Weight of Sample.	Combustibility k measured at the same temperature 930°C.
Parallelo-piped.	Length - 2.22 Breadth - 2.22 Height - 2.85	3.49	4.000
Sphere	Diameter - 3.01	2.68	3.735
Cylinder	Length - 3.33 Diameter - 3.17	2.45	3.700
Cylinder	Length - 2.85 Diameter - 2.54	2.38	3.540
Cylinder	Length - 3.81 Diameter - 2.86	2.37	3.429

Figs. 23 and 24, since the curvature at the ignition range is not shown. Experimental difficulties make the quotation of combustibilities in this range impossible since temperature oscillations of even 5°C on either side of the experimental temperature can make differences out of all proportion to the amount of temperature fluctuation, e.g., for Coke E the combustion of 1.5 grams takes 34 minutes at 710°C compared with 7 minutes at 725°C under similar conditions. Although the conditions at ignition have not been fully illustrated, it will be seen that measurements have been made at temperatures outwith the ignition range for higher rates of air supply, i.e., at temperatures too low to allow of measurement of combustibility with high rate of air blast.

The results of experiments showing the effect of shape and dimensions of the coke specimen as affecting combustibility are given in Table 24, (31). These experiments were performed with samples of Coke D and manufactured graphite and the pertinent data of the combustibility test is given in the same Table. The ratio of calculated superficial area to original weight of the sample has been used as a measure of the various dimensional and geometrical changes of the standard test piece, and Table 24 proves that the higher this ratio the greater the combustibility, although the limits of the ratio are not sufficiently far apart to merit mathematical treatment. Some such dependence of combustibility upon the shape and dimension of the standard sample was to be expected, and it was for this reason that the standard sample of this type of test was arbitrarily fixed from the start. The reasons for the particular choice of shape and dimensions have already been delineated in the description of the apparatus.

There are several obvious gaps in both theory and experiment which still require elucidation. Several of these unknowns have been determined in Chapter 3. Others will have to wait on the researches of pure physicists and mathematicians, but the author considers that with a proper allowance for the complexi-

ties of the problem, the problem of combustion has been brought into a true focus. Coke (and this applies to other solid fuels) has not been considered as an exceptional solid obeying exceptional rules. The reaction

$$C_{solid} + O_{gas}$$

is a chemical reaction subject to the same laws as every other chemical reaction requiring only a knowledge of the fundamental constants. The identity of these constants has been indicated in this Chapter and will be added to in Chapter 3. The further possibilities of controlling these constants in industrial processing of coal form the subject matter of Chapter 3.

CHAPTER THREE.

The effect of the variables of carbonisation on combustibility.

The deficiencies of industrial cokes as standards for the accurate determination of general laws relating the physico-chemical constants of solid fuels to combustibility are obvious. By carbonising on a controlled laboratory scale, the indeterminate conditions of industrial coking are avoided, but even more important is the achievement of uniformity and reproducibility of an infinite variety of cokes by the permutation of the known variables of coking practice. It is the purpose of this Chapter to discuss the singular effect of each of these variables on combustibility and on the macroscopic physical features of cokes.

The apparatus of Fig. 25 was designed to produce cylindrical coke blocks sufficiently long to provide two test pieces as duplicate standards for the combustibility test and a further sample for proximate analysis. As a precaution against the excessive scaling of the steel container of Fig. 25, a current of coal gas was continuously passed through the Pythagoras tube, and with the gases evolved by the coal charge during carbonisation, was burned at the mouth of the copper tube chimney. The other features of Fig. 25 are self-explanatory.

Three varieties of coal of widely differing origin, chemical composition and petrographical distribution were used in the preparation of five series of cokes, particularised below. The analyses and other relevant data of the coal bases are given in Table 25. Each coal supply ($\frac{1}{4}$") was halved according to standardised sampling practice. One of these portions was ground to pass 72 mesh B.S.S. from which basic source, samples of 80 grams were packed in the steel or alundum container to give the same bulk density or packed volume each time. Such charges were then -

Fig.25.

Details of Carbonising Furnace.

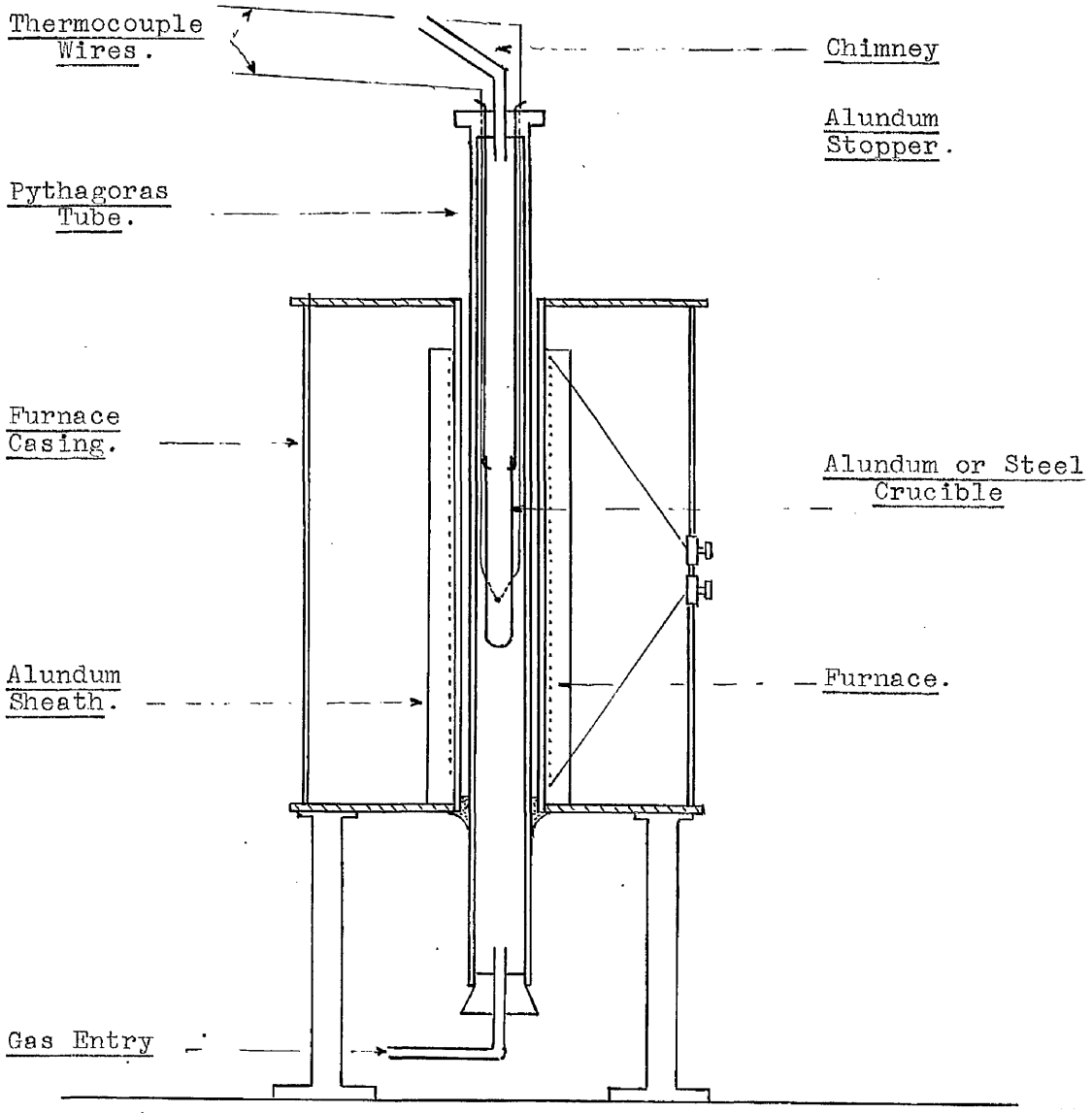


TABLE 25.

Analyses of the Coals used in the preparation of the Coke series.

Proximate Analysis.	Coal A.	Coal B.	Coal C.
Moisture.	2.3	1.4	1.5
Volatile Matter less Moisture.	39.6	24.5	21.4
Fixed Carbon.	54.9	64.2	62.0
Ash.	3.2	9.9	15.1
Ultimate Analysis.			
Ash.	3.28	10.04	15.37
Carbon.	81.71	77.96	73.97
Carbon (as CO_3)	0.04	0.06	0.04
Hydrogen	5.60	4.43	4.50
Nitrogen.	1.66	1.48	1.75
Sulphur (Total).	0.74	0.63	0.58
Difference (Oxygen and errors).	6.97	5.40	3.29
Colour of Ash.	Pale pink.	Buff.	Light buff.

Character of Coke Button.

For Coal A. Silver grey, lustrous, dull patch at centre, swollen smooth surface, slightly fissured, cellular, hard.

For Coal B. Dark grey, very slight lustre, slightly swollen, fissured, cellular, hard.

For Coal C. Silver grey, lustrous, swollen, slightly fissured, cellular, hard.

(a). heated from room temperature to temperatures of 500°C to 1200°C at 100°C intervals at 5°C per minute, and maintained at the proposed final temperature for 1 hour.

(b). heated as in (a), but at the rate of 3°C per minute.

(c). heated from room temperature to 900°C at 5°C per minute, but varying the time of soaking at that temperature for times up to 12 hours.

(d). added to the steel pot, which is heated initially to temperatures from 200°C to 800°C. After charging, the heating is continued to 900°C as in (a).

The second portion of the original coal supply was divided into six parts. Each of these was ground in such a way as to ensure the maximum amount of material just passing the specified sieve.

(e). With special precautions to secure the same packing for all particle sizes, the usual 80 gram sample from each of these six portions is heated to 900°C under the conditions of (a).

In all the above series, the coke was allowed to cool in the furnace. The test pieces for combustion were cut from the 6 inch cylindrical blocks, trimmed to the arbitrary standard dimensions for the combustibility test and burned at temperatures of 850°C and 950°C under a constant rate of air supply of 102.4 cb.ft./hour (N.T.P.) supplied at 15 lbs./sq.in. at the inlet to the Pythagoras tube. The proximate analyses of the individual samples of the series of cokes prepared from each of the coals by operations (a) to (e) are given in Tables 27 to 31 inclusive. Besides the analytical details, the observed values of combustibilities of the cokes at 850°C and 950°C are recorded, and these are graphically represented in Figs. 29 to 34.

It is advisable to introduce at this stage the theoretical considerations and experimental evidence which led to the proposed co-ordination of the results of the above combustibility tests. In the previous Chapter, the author has stressed the indefinite nature of the term "coke", in that it is applied to all the products of an irreversible thermal process of infinite variability; products, the physico-chemical stability of which depend upon the conditions of their subsequent use.

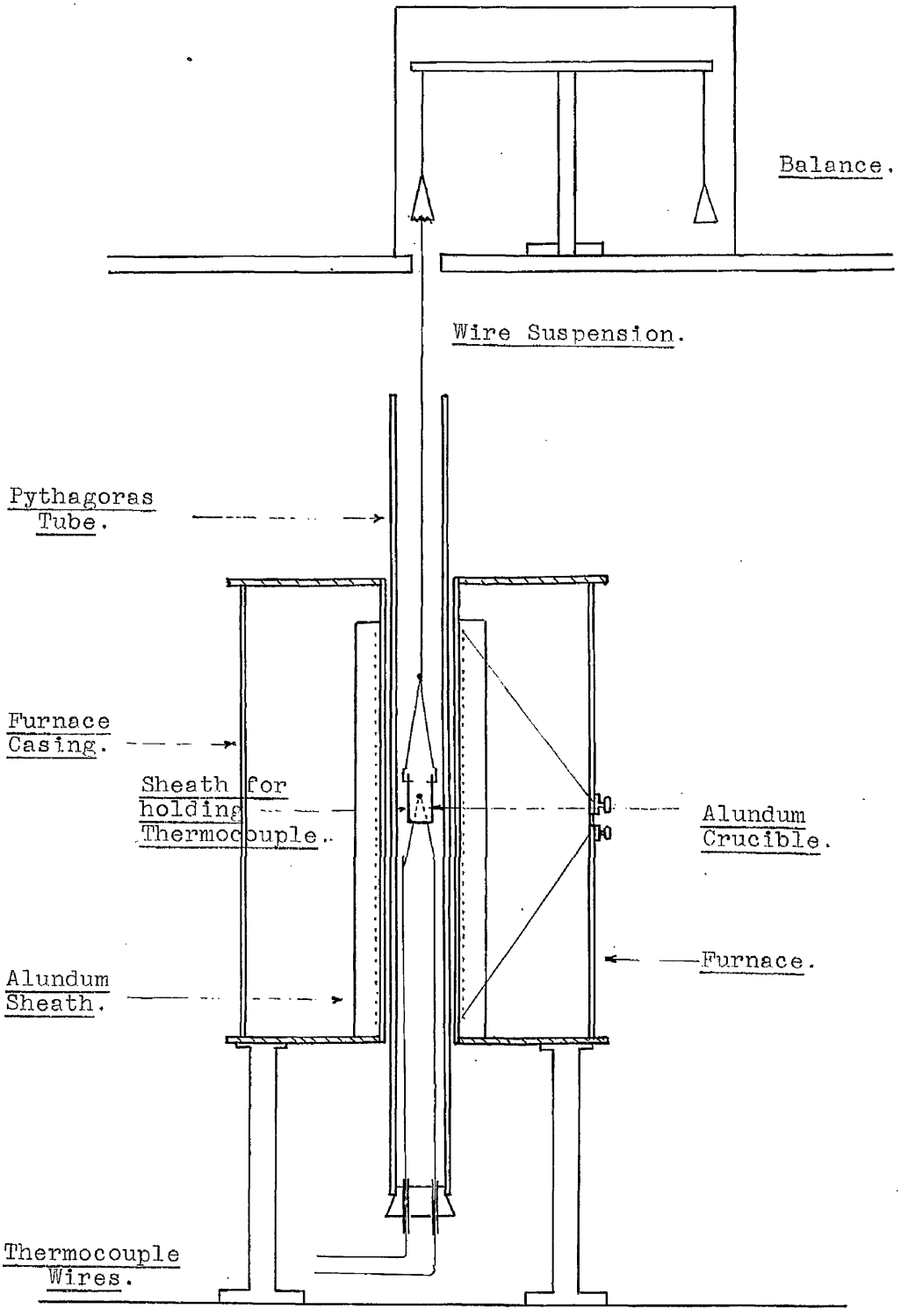


Fig. 26.

Apparatus for Measuring Weight Changes in Coal on Carbonisation.

No quotation of combustibility can be of value, therefore, if the temperature of combustion is not given, since the probable stability of any coke is in some measure determined by the positive or negative difference between its coking temperature and the temperature of combustion. By considering the positive difference, the author allows for a possible continuous internal activity of the cokes not evidenced by the experimental limitations of the combustibility test, e.g., graphitisation. The temperature of combustion is, therefore, a transition temperature dividing a region of pronounced instability, i.e., cokes prepared at temperatures below the temperature of combustion, from one of lesser allotropic activity.

To measure the changes in the coal base on carbonisation, the apparatus of Fig. 26 was constructed (32). A modified form of the combustibility test, it was designed to weigh continuously the loss by volatile emission of the organic constituents of the coking coal. The curves of Figs. 27 and 28 are graphical records of the progress of carbonisation of 15 gram sample of coals A and C heated from room temperature to 800°C at 5°C/minute and 3°C/minute. The ordinate of the curves is the difference in weight between consecutive observations. The experimental method does not distinguish between the various simultaneous chemical reactions peculiar to the coal base, and which combine to give the complex curves of Figs. 27 and 28.

For all these curves of coke formation, the temperature of the maximum loss of moisture (100°C) is unaffected by the rate of heating of the coal charge. From 200°C, the curves of the separate figures, although similar in type, diverge, with the curves for the slower rate of heating showing less pronounced maxima of gas evolution displaced in the temperature axis towards the origin. The minimum temperature of organic volatilisation as determined by these curves is the start of an irreversible chemical activity - an activity which is neither instantaneous nor uniform in either volume and content.

Fig. 27.

The Progress of Carbonisation of Coal C.

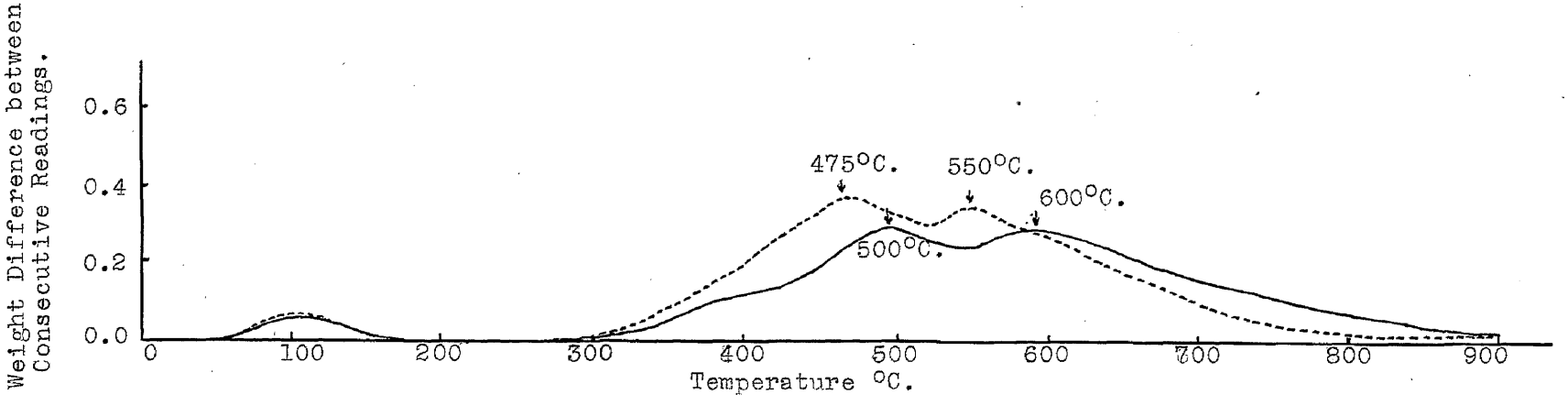
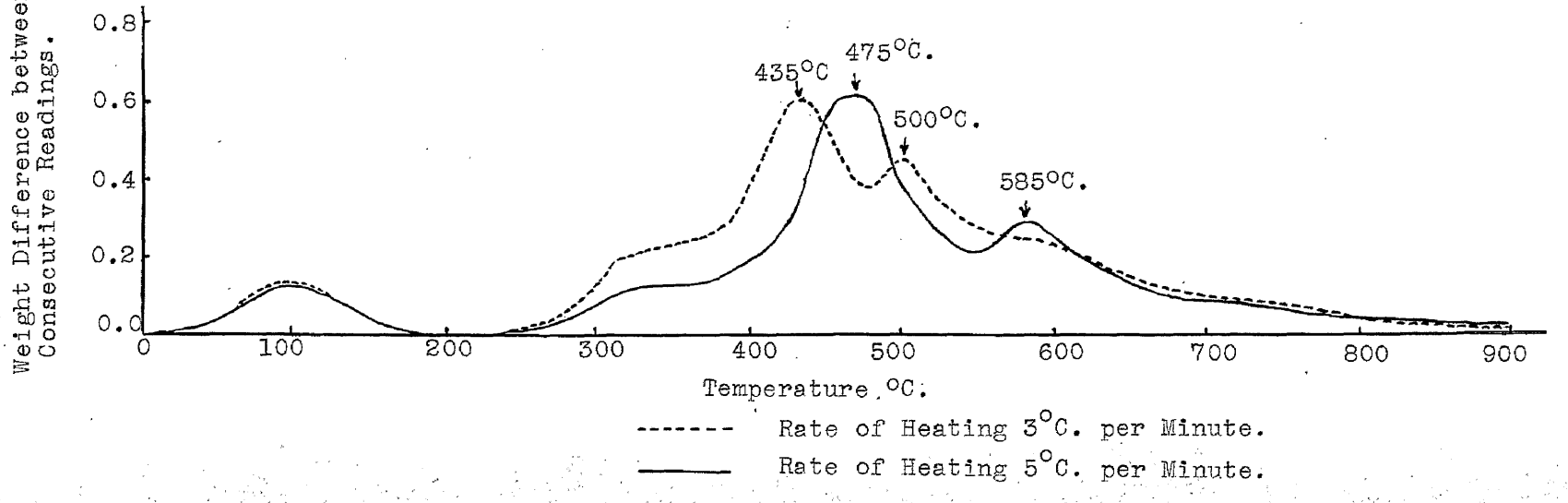


Fig. 28.

The Progress of Carbonisation of Coal A.



Whereas the onset of carbonisation can be accurately estimated, its completion is indefinite since, as the phenomenon of re-carbonisation (see Chapter 1) showed, volatile emission is continuous to the highest temperatures. By this experimental method, however, the loss due to recarbonisation (mainly hydrogen and nitrogen)(7) is negligible compared with that of the essentially organic discharge of carbonisation. For convenience, therefore, the minimum temperature of nearest approach of the carbonisation curve to the temperature axis will be considered as approximately defining the end of carbonisation, but not the cessation of all chemical activity.

All the carbonisation range is not equally significant in its influence on coke formation or coke combustibility. Two regions can be distinguished. There is the caking and/or plastic range, the distinctive characteristic of which is the elimination of the individual physical features of the coal charge. The temperature limits of this range are the temperatures of gelatinous liquefaction and later solidification of the coal base, and these are conditioned by the organic compounds of the coal, the rate of carbonisation and the particle size of the coal charge. The rate of gaseous volatilisation and exhaustion in this range are the sole factors determining the absolute value of combustibility of the resulting solid semi-coke. The combustibility of a partially carbonised coal charge, obtained by interruption of the carbonisation within the plastic range, discontinuously decreases with increasing temperature to the limit of the plastic range. Only by the control of the variables of carbonisation within the region of plasticity can the "hereditary" (and desirable) characteristics of the rigid cellular structure of coke be acquired. The solid semi-coke of the end of the plastic range is the transition phase of the second region of carbonisation. The fundamental and persistent characteristics of this basic coke can be modified both chemically and physically by further heat treatment in this range. This results from the continued evolution of

the remaining organic volatile matter accompanied by shrinkage and/or fissuring (33). Neglecting the complicating inconsistencies of mechanical rupture on combustibility, which have already been discussed for anthracite (see Chapter 2), this mutability of coke has but one effect on the rate of combustion - a continuous decrease of its value to some minimum with increasing time and temperature of coking, demonstrated by the combustibility curves of cokes made by operations (a) to (d), Figs. 29 to 33.

The graphs of Figs. 29 and 30 and the relevant proximate analyses of Tables 26 and 27 illustrate the effect of the maximum temperature of coking and the rate of carbonisation on combustibility (7,33,34,35,36,37). Although all these curves are of the same type, no mathematical formula has been found, as yet, to correlate the combustibility k_T with the variables of coking under discussion. For any one series of cokes, the combustibility k_T and the volatile content on a dry ash free basis decrease asymptotically to a minimum value with increase in the coking temperatures investigated. This similarity in coke behaviour explains the obvious combustibility variations with coking temperature on the assumption that the greater the volatile matter of a coke, the greater its combustibility. Such a dependence has been noted already for the conditions of the plastic range. Since the effect of increasing coking temperature can only be to reduce or maintain the volatile content, this dependence of combustibility on volatile content accounts for the shape of the curves of Figs. 29 and 30. The absolute value of the volatile matter in itself is not, however, a basis of comparison for the relative combustibilities of cokes prepared from different coal sources, since this takes no account of the chemical nature of the coal constituents or of its later decomposition (29).

That there is no direct proportionality between combustibility and volatile matter for any of the coke series cannot be attributed solely to the standard method of estimation of

Fig. 29.

The Effect of Maximum Temperature of Coking and Rate of Carbonisation on Combustibility.

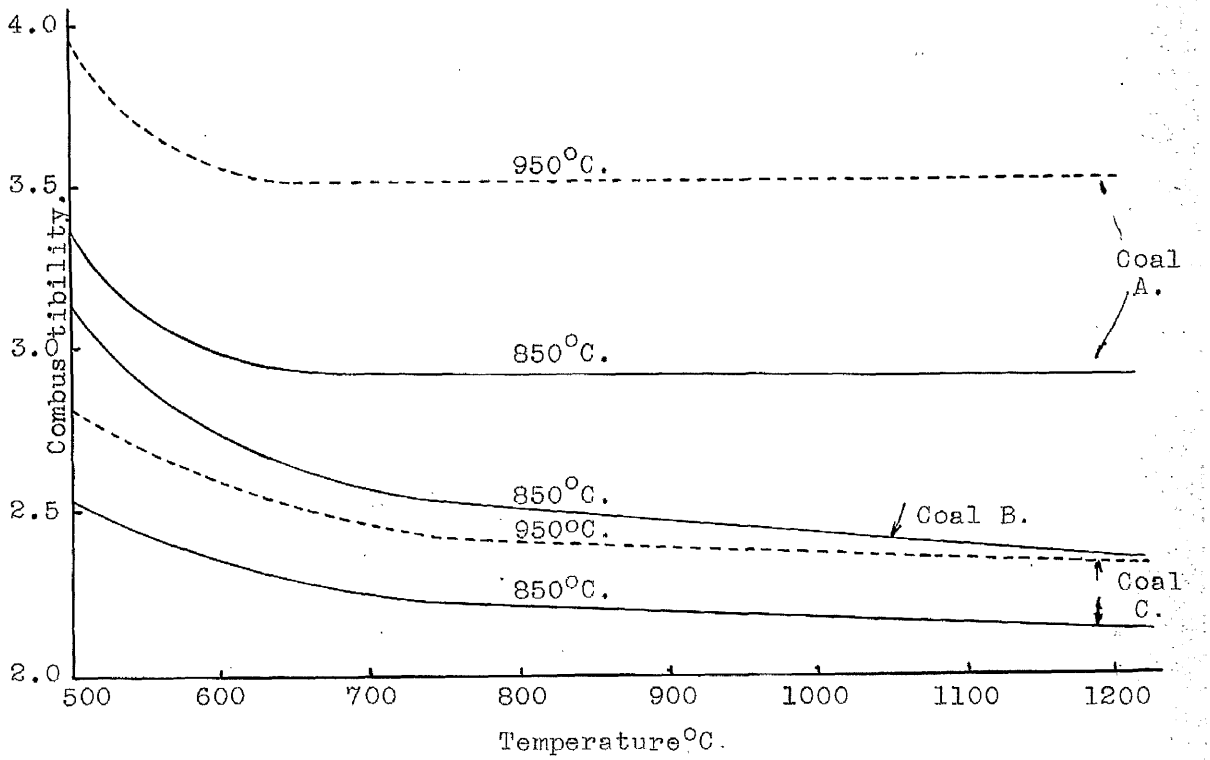


Fig. 30.

The Effect of Maximum Temperature of Coking and Rate of Carbonisation on Combustibility.

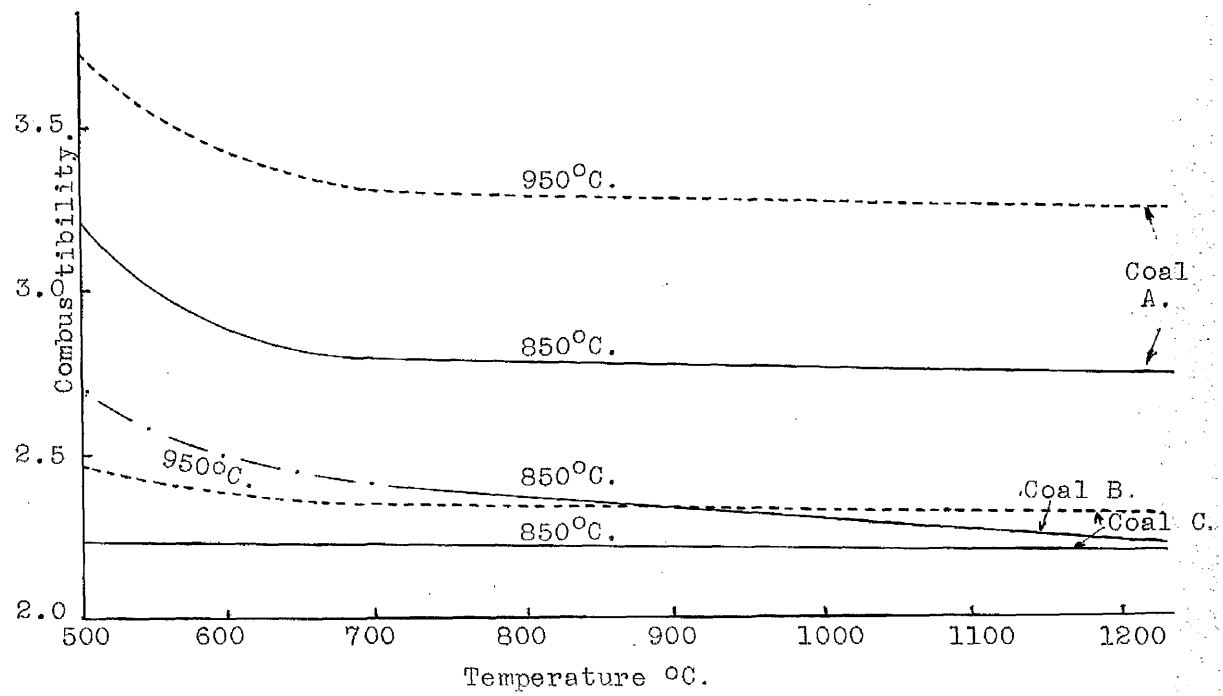


Figure on Curve denotes Temperature of Combustion.

TABLE 26.

Analyses of the series of Cokes prepared to show the effect of maximum temperature of Coking and rate of carbonisation.

Rate of heating to maximum temperature - 5°C./minute.
Time of soaking at maximum temperature - 1 hour.

COAL A.

Maximum Temp. of Coking.	500°C.	600°C.	700°C.	800°C.	900°C.	1000°C.	1100°C.	1200°C.
Moisture.	2.7	3.1	4.3	4.9	4.4	1.4	0.7	0.1
Volatile Matter less moisture.	29.2	26.2	10.1	5.1	3.9	2.6	1.6	0.9
Fixed Carbon.	63.5	66.5	81.0	85.1	87.1	91.0	92.7	94.0
Ash.	4.6	4.2	4.6	4.9	4.7	5.0	5.0	5.0
Volatile Matter. dry ash free.	31.5	28.2	11.1	5.7	4.3	2.8	1.7	1.0
Combustibility at 850°C.	3.400	2.954	2.928	2.937	2.910	2.920	2.940	2.920
Combustibility at 950°C.	3.944	3.530	3.520	3.500	3.520	3.545	-	3.526

COAL B.

Maximum Temp. of Coking.	500°C.	600°C.	700°C.	800°C.	900°C.	1000°C.	1100°C.	1200°C.
Moisture.	1.9	3.2	3.9	4.5	4.3	1.5	0.5	0.3
Volatile Matter less moisture.	12.3	7.8	7.0	5.5	3.6	1.6	1.0	0.8
Fixed Carbon.	74.1	77.4	77.4	78.2	80.5	85.0	86.0	86.4
Ash.	11.7	11.6	11.7	11.8	11.6	11.9	12.5	12.5
Volatile Matter. dry ash free.	14.2	9.2	8.3	6.6	4.3	1.8	1.1	0.9
Combustibility at 850°C.	3.125	2.781	2.536	2.522	2.500	2.422	2.385	2.330
Combustibility at 950°C.			-					

COAL C.

Maximum Temp. of Coking.	500°C.	600°C.	700°C.	800°C.	900°C.	1000°C.	1100°C.	1200°C.
Moisture.	1.5	2.4	3.1	3.6	1.7	0.3	0.1	0.3
Volatile Matter less moisture.	12.4	8.4	4.7	3.3	1.6	0.8	0.9	0.5
Fixed Carbon.	70.0	72.6	75.3	76.4	78.9	81.0	81.3	82.1
Ash.	16.1	16.6	16.9	16.7	17.8	17.9	17.7	17.1
Volatile Matter, dry ash free.	15.0	10.4	5.9	4.1	2.0	1.0	1.1	0.6
Combustibility at 850°C.	2.538	2.375	2.241	2.200	2.200	2.172	2.143	2.138
Combustibility at 950°C.	2.815	2.607	2.548	2.444	2.364	2.355	2.352	2.344

TABLE 27.

Analyses of the series of Cokes prepared to show the effect of maximum temperature of coking and rate of carbonisation.

Rate of heating to maximum temperature - 3°C./minute.
Time of soaking at maximum temperature - 1 hour.

COAL A.

Maximum Temp. of Coking.	500°C.	600°C.	700°C.	800°C.	900°C.	1000°C.	1100°C.	1200°C.
Moisture.	2.7	3.2	4.5	4.8	4.7	1.4	0.3	0.1
Volatile Matter less moisture.	28.1	20.2	6.9	5.6	3.8	2.0	1.6	0.6
Fixed Carbon.	64.8	72.0	83.7	85.1	87.1	92.0	93.5	94.3
Ash.	4.4	4.6	4.9	4.5	4.4	4.6	4.6	5.0
Volatile Matter, dry ash free.	30.3	21.8	7.6	6.2	4.2	2.1	1.7	0.7
Combustibility at 850°C.	3.220	2.856	2.808	2.770	2,780	2.787	2.780	2.740
Combustibility at 950°C.	3.700	3.444	3.364	3.320	3.333	3.260	3.240	3.240

COAL B.

Maximum Temp. of Coking.	500°C.	600°C.	700°C.	800°C.	900°C.	1000°C.	1100°C.	1200°C.
Moisture.			4.4	4.9	4.1	2.2	1.2	0.1
Volatile Matter less moisture.			7.5	6.1	2.9	1.6	1.5	0.6
Fixed Carbon.			76.4	77.1	82.2	83.7	83.9	86.2
Ash.			11.7	11.9	10.8	12.5	13.5	13.1
Volatile Matter, dry ash free.			8.9	7.3	3.4	1.9	1.8	0.7
Combustibility at 850°C.			2.406	2.353	2.320	2.300	2.281	2.222
Combustibility at 950°C.								

COAL C.

Maximum Temp. of Coking.	500°C.	600°C.	700°C.	800°C.	900°C.	1000°C.	1100°C.	1200°C.
Moisture.	1.6	2.3	3.2	3.6	1.7	0.2	0.2	0.2
Volatile Matter less moisture.	10.9	6.9	5.2	4.1	1.9	0.9	0.8	0.6
Fixed Carbon.	71.5	73.8	74.3	74.4	78.3	80.3	80.5	81.3
Ash.	16.0	17.0	17.3	17.9	18.1	18.6	18.5	17.9
Volatile Matter, dry ash free.	13.2	8.6	6.5	5.2	2.4	1.1	1.0	0.7
Combustibility at 850°C.	2.250	2.220	2.212	2.166	2.148	2.143	2.143	2.125
Combustibility at 950°C.	2.465	2.420	2.387	2.378	2.341	2.320	2.320	2.320

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volatile matter, which is only approximate for cokes prepared above 1000°C. A more probable explanation is the postulation of a consecutive secondary reaction to volatile emission, the allotropic reaction

Carbon --> Graphite

for which other evidence exists (8). The initial temperature of transformation is doubtful. The presence of elements other than carbon in the carbonised complex will inhibit graphitisation, but with no apparent discontinuity in the combustibility/coking temperature curves, there is no reason to suppose that the phase change does not start at, or slightly above, the beginning of the second of the regions of carbonisation (37, 38). The distinctive feature of increasing graphitisation of coke is the reduction of combustibility, and the combustibility of completely graphitised coke is the asymptotic value to which all cokes of comparable preparation tend (35).

For the two series of cokes prepared at different rates of carbonisation from each of the coals, the combustibility/coking temperature curve is progressively depressed in the combustibility axis with decrease of the rate of carbonisation. This could be an effect of the time of coking (see below), which for the same final temperature by a slower rate of heating increases proportionately the degree of volatile emission and graphitisation, with the consequent decrease in its relative combustibility to one of quicker heating. Were this the only factor, however, the curves of combustibility for cokes prepared at the two different rates should tend to coincide at some temperature where chemical activity is almost complete, but this the parallelism of the pairs of curves of Figs. 29 and 30 in the higher regions of temperature disproves. Therefore, rate of carbonisation itself is a determining condition of combustibility. In the description of the conditions of the plastic range, reference was made to the controlling factor of the rate of gaseous volatilisation, and that this is a function of the rate of heating is obvious on a

comparison of the carbonisation curves of Figs. 27 and 28, whose differences are reflected in the basic coke at the end of the plastic range in differences of cellular structure, which survive any heat treatment at and above the temperatures of these experiments. It must be emphasised that control of the variables of coke formation is only effective, when exerted in the plastic range. The changes outside this range merely modify existing conditions, but do not create new physical features. Reference to this will be made in the discussion of the effect of coal particle size on coke formation.

Finally, the lower the average ash content of the coke series, the higher the position of the curve of combustibility/coking temperature in the ordinate axis of combustibility. The diluent effect of ash by reducing the combustible surface area reduces the rate of combustion. Whether the amount of reduction is equivalent to the amount of ash, treated as a neutral passive constituent, or whether possible catalytic activity may play a part still remains to be proved. Conditions at ignition appear to be sensitive to inorganic additions, e.g., lime (31, 34).

From the analytical aspect of the cokes of (a) and (b), one observation is worth comment. The moisture content of any of the series of cokes rises to a maximum at a coking temperature of 800°C. The curve is typically represented in Fig. 30 and is of the form

$$y_{H_2O} = AT_c^{-ax} + BT_c^{-bx}$$

where y_{H_2O} is the moisture content and T_c the maximum coking temperature. a,b,A and B are constants, the particular values of which are not given here. The absolute values of comparable cokes is independent of the rate of heating. The unforeseen and consistent interdependence of the moisture content of a coke and the maximum temperature of coking appears to be one more example of the discriminate superficial adsorptive capacity of cokes for gases and liquids. It may be more than

Fig. 31.

The Relation between Coke Moisture and Maximum Temperature of Coking.

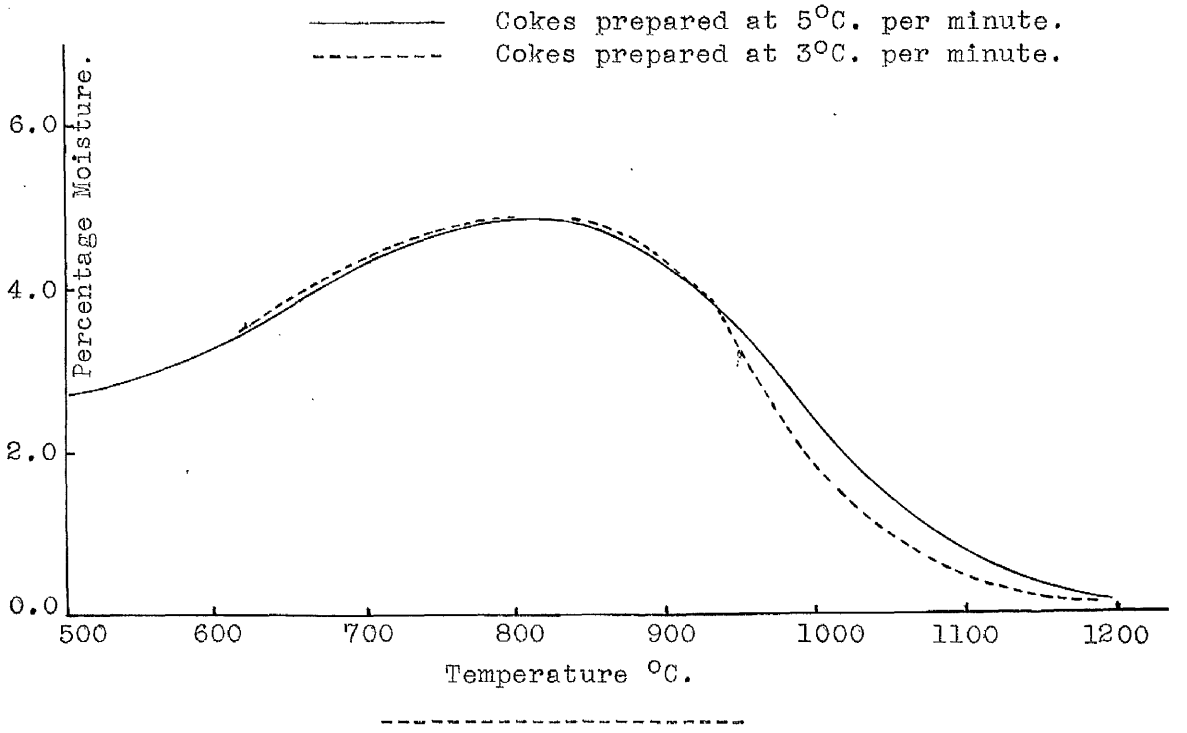

Fig. 32.

The Effect of Time of Coking on Combustibility.

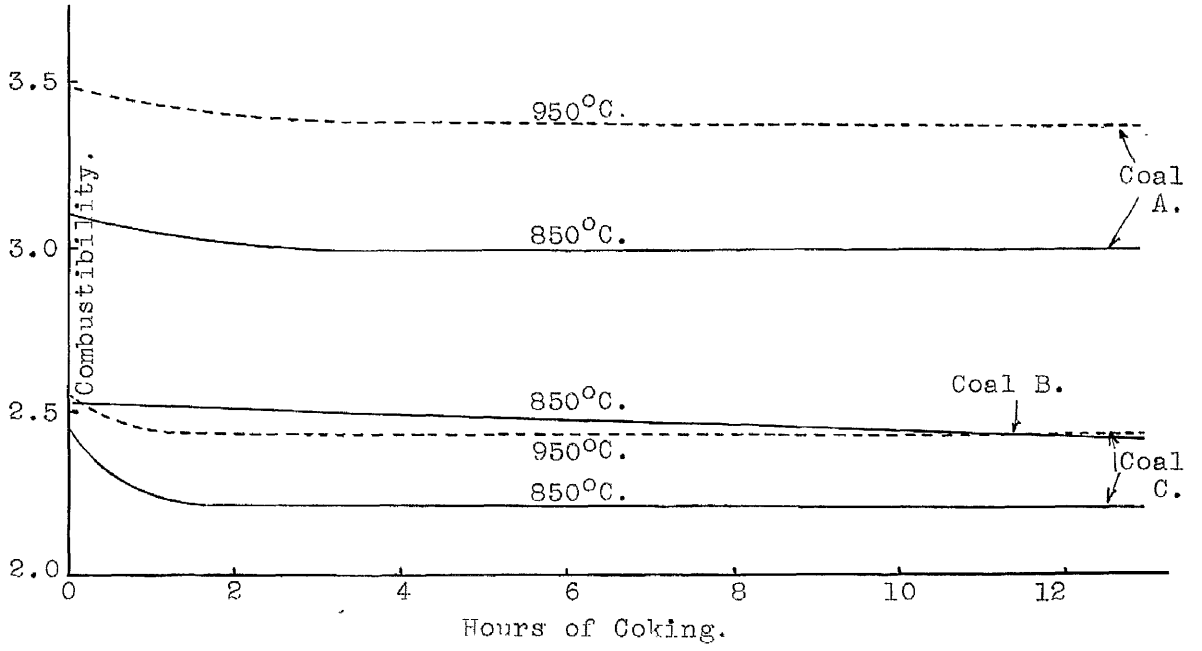

Figure on Curve denotes Temperature of Combustion.

TABLE 28.

Analyses of the series of Cokes prepared to show the effect of time of Coking.

Rate of heating to maximum temperature - 5°C/minute.
Maximum temperature - 900°C.

COAL A.

Time of Coking.	0 hrs.	¾ hrs.	1½ hrs.	3 hrs.	6 hrs.	12 hrs.
Moisture.	4.2	4.1	4.5	4.3	3.3	0.9
Volatile Matter less moisture.	4.3	4.3	3.8	4.4	2.8	1.9
Fixed Carbon.	86.6	86.8	86.8	86.8	91.3	92.5
Ash.	4.9	4.8	4.9	4.5	4.6	4.7
Volatile Matter, dry ash free.	4.7	4.7	4.2	4.8	3.1	2.0
Combustibility at 850°C.	3.104	3.080	2.940	3.000	3.000	3.000
Combustibility at 950°C.	3.460	3.435	3.460	3.423	3.366	3.375

COAL B.

Time of Coking.	1 hr.	3 hrs.	6 hrs.	9 hrs.	12 hrs.
Moisture.	3.9	1.1	0.9	1.1	1.6
Volatile Matter less moisture.	2.8	1.8	1.5	1.8	1.8
Fixed Carbon.	82.1	85.2	85.8	85.3	84.1
Ash.	11.2	11.9	11.8	11.8	12.5
Volatile Matter, dry ash free.	3.3	3.1	1.7	2.1	2.1
Combustibility at 850°C.	2.520	2.515	2.460	2.450	2.436
Combustibility at 950°C.	2.800	2.750	2.740	2.730	2.730

COAL C.

Time of Coking.	0 hrs.	¾ hrs.	1½ hrs.	3 hrs.	6 hrs.	12 hrs.
Moisture.	2.7	2.4	2.1	0.6	0.3	0.3
Volatile Matter less moisture.	2.5	1.9	2.0	1.2	1.0	0.8
Fixed Carbon.	77.1	78.1	78.2	80.3	80.8	80.8
Ash.	17.7	17.6	17.7	17.9	17.9	18.1
Volatile Matter. dry ash free.	3.1	2.4	2.5	1.5	1.2	1.0
Combustibility at 850°C.	2.500	2.241	2.235	2.235	2.222	2.225
Combustibility at 950°C.	2.560	2.430	2.430	2.440	2.445	2.430

coincidence that the optimum effect for the maximum adsorption of oxygen by recarbonised cokes occurs at or about 800°C, (7), (See Chapter 1). The similarity of the values of moisture for the comparable series of Tables 26 and 27 would indicate that the intermediate stages of coke formation do not affect the adsorptive capacity of the final product.

The curves of Fig. 32 and the analyses of Table 28 illustrate the effect of time of coking on combustibility (36, 37). Generally, by increasing the time of coking at any temperature the combustibility of any coke is continually reduced to, or at best maintained at, some minimum value. This value is the combustibility k_G of the completely graphitised coke, ultimately obtained by an indefinite period of heating at any temperature above the transition temperature of carbon/graphite. The time of heating required to affect comparable degrees of graphitisation in any type of coke is decreased by increasing the temperature of coking. The relative effects of time and temperature in reducing combustibility may be judged by the experience of Coal B, where, burning at 850°C, a difference of 300°C in coking temperature, (1200°C to 900°C) can make approximately twice the difference in combustibility to be obtained by a heat treatment of 12 hours at 900°C. The inconsistent variation of the volatile content with time of coking cannot explain, as in the previous discussion, the continuous reduction in combustibility. Thus, with increasing times of coking graphitisation assumes a greater importance. The arbitrary choice of one hour as the time of soaking for the experimental work of previous operations was adopted for convenience.

The single curve of Fig. 33 and the proximate analyses of its individual cokes for the single coal C was not repeated for the other two coals (Table 29). From this graph, the higher the charging temperature of the coal, the greater the combustibility of the coke produced for the same final temperature. The curve is virtually a combination of the single variables of the

TABLE 29.

Analyses of the single series of Cokes prepared to show the effect of an increasing initial temperature of charging.

Rate of heating to maximum temperature - 5°C. per minute.
Time of soaking at maximum temperature - 1 hour.

COAL C.

Initial Temperature of Charging.	20°C.	200°C.	400°C.	600°C.	800°C.
Moisture.	1.7	1.5	0.5	1.1	0.9
Volatile Matter less moisture.	1.6	2.2	1.2	1.9	1.3
Fixed Carbon.	28.9	77.7	79.9	78.5	79.4
Ash.	17.8	18.6	18.4	18.5	18.4
Volatile Matter, dry ash free.	2.0	2.8	1.5	2.4	1.6
Combustibility at 850°C.	2.200	2.468	2.961	3.444	3.643

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previous operations and confirms the relationships, already recorded, of these variables to combustibility. Since control of the conditions in the plastic range are determined by the temperature of charging, the higher this temperature the greater the rate of carbonisation and the consequent improvement in the value of combustibility. Incidentally, the time to attain the final coking temperature of 900°C is lessened by increasing the temperature of charging, thus relatively increasing still further the differences of combustibility occasioned by the variable rate of carbonisation. The exceptional behaviour of the coke of initial heating temperature 800°C is the result of uncontrolled preparation, the experimental difficulties of this type of coke production multiplying with increasing charging temperature. The physical appearance of this coke differs from that of the others, being a solid shell ($\frac{1}{4}$" thick) surrounding a hollow thinly filled core. The estimated combustibility of the outer denser rim is lower than would be the case for a more uniformly coked mass, but the production of such a coke must await larger scale research.

The curves of Fig. 34 and the analyses of the cokes, prepared as in operation (e) of Table 30, illustrate the effect of particle size of the coal charge on combustibility (25). By plotting the results on the scale of Fig. 34 it is intended to emphasise the selection of sieves, each screen passing a particle of a diameter twice that of its immediate neighbour in the sequence. The procedure for grinding was regulated to produce the maximum amount of material just passing a specified sieve, but the restriction of the fines to particular limits was impossible. Lacking a screen analysis of the ground samples, the quotation of the upper screen limit has been used as a convenient distinction between the <u>average</u> particle coal sizes of the various charges. The unavoidable production of a range of sizes on grinding introduces subsidiary complicating factors, e.g., packing, interstitial filling, etc., which may affect carbonisation but this series of experiments neither differentiates

Fig. 33.

The Effect of Initial Charging Temperature on Combustibility.

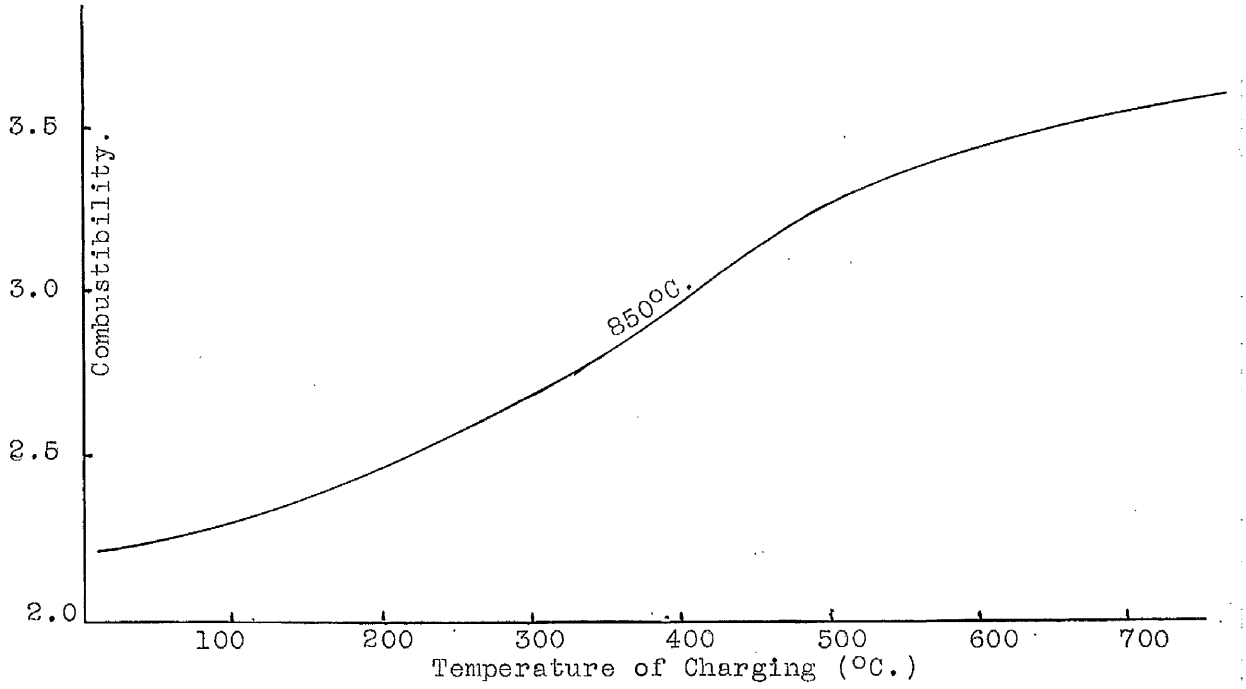

Fig. 34.

The Effect of Particle Size of the Coal Charge on Combustibility.

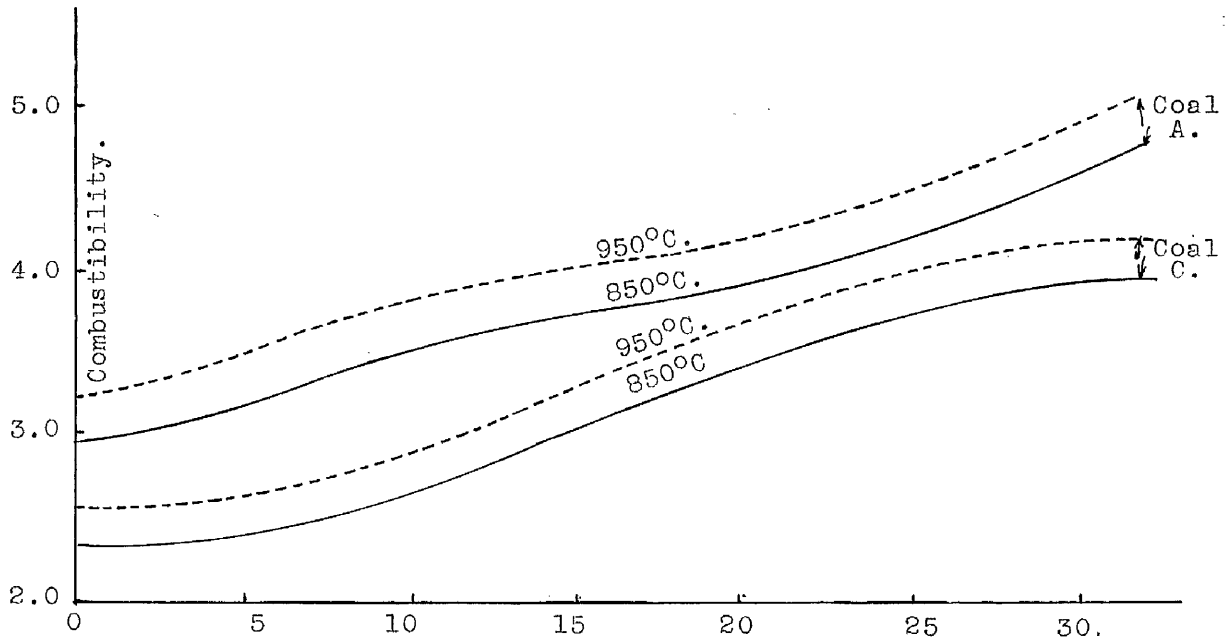

Figure on Curve denotes temperature of Combustion.

TABLE 30.

Analyses of the Series of Cokes prepared to show the effect of the particle size of the charge.

Rate of heating to maximum temperature - 5°C./minute.
Time of soaking at maximum temperature - 1 hour.

COAL A.

Maximum Particle Size (B.S.S.)	5	10	18	36	72	150
Moisture.	3.6	3.5	4.6	4.9	4.4	4.4
Volatile Matter less moisture.	3.7	3.7	3.8	4.3	3.9	4.0
Fixed Carbon.	88.2	88.1	87.2	86.2	87.0	86.6
Ash.	4.5	4.7	4.4	4.6	4.7	5.0
Volatile Matter, dry ash free.	4.0	4.0	4.2	4.8	4.3	4.4
Combustibility at 850°C.	4.781	3.750	3.500	3.120	2.910	2.960
Combustibility at 950°C.	5.108	4.058	3.761	3.333	3.520	3.350

COAL C.

Maximum Particle Size (B.S.S.)	5	10	18	36	72	150
Moisture.	1.5	1.5	1.6	1.8	1.7	1.9
Volatile Matter less moisture.	3.4	3.1	3.0	3.7	3.0	3.5
Fixed Carbon.	76.1	76.0	75.7	75.8	76.7	74.4
Ash.	19.0	19.4	19.7	18.7	18.6	20.2
Volatile Matter, dry ash free.	4.3	3.9	3.8	4.7	3.8	4.5
Combustibility at 850°C.	4.000	3.150	2.500	2.400	2.353	2.341
Combustibility at 950°C.	4.333	3.316	2.846	2.632	2.530	2.520

between the individual factors nor evaluates their relative importance. To minimise their effects, the bulk density (or packing) of each charge is adjusted to the same level as for previous operations using the same original coal.

The effect of this essential variable of carbonisation is to produce cokes of increasing combustibility from coal charges of increasing particle size. The curves of Fig. 34 show that this tendency is less pronounced and approaches (by lesser absolute differences of size on reduction in geometric progression) a minimum value of combustibility for the coal charges of fine material, approximately - 72 mesh B.S.S. Above this screen, however, a change of size is of greater moment in its effect on coke formation (and hence coke combustibility) than probably any of the other factors previously discussed, e.g., a fourfold increase in mesh size from 18 B.S.S. to 5 B.S.S. involves a 50% increase in combustibility on the lower value. The differences in the properties of cokes prepared from the same coal under the same thermal conditions are the consequence of macroscopic structural differences created in the plastic range of carbonisation by the less well defined temperature limits of liquefaction and lesser turbulence of gaseous evolution obtaining with increasing dimensions of the coal particle. Alternatively, since the instantaneous activity of a coal charge in the plastic range is the sum of the activity of each individual particle, the ratio of the volume of the particle to its surface area is probably the determining factor of coke formation. A similar ratio has been found to influence the combustibility value of any coke (See Chapter 2). The greater this ratio of the average particle of the coal charge, the greater is the combustibility of the resulting coke, all other conditions being assumed equal.

The combustibility curves at 850°C and 950°C for each of the coke series are not parallel in the region of greater particle size, and this is probably due to the difficulty of preparing uniform coke blocks from the larger sizes of coal

particles with its variable interstitial filling. Where by size reduction and proper mixing, local peculiarities are eliminated, the difference in combustibility at the two temperatures for cokes prepared from the finer charges remains sensibly constant.

Advantage has been taken of the differences in abradability of the petrographical constituents of a coal to indicate the inherent differences in combustibility of various proportions of these constituents, or rather of the cokes produced from them. Coal B "as received" was ground, screened between various mesh limits and these portions coked under the conditions of Table 31, which also gives the proximate analyses of the cokes thus prepared. Both the analyses and combustibilities vary considerably from that of the unscreened 72 mesh B.S.S. coal, but no definite relationship has been established. The experiment does suggest the possibility of screen elutriation as a method of controlling carbonisation and/or combustibility.

The primary measure of the combustibility of any coke has been shown to originate in the plastic range of carbonisation, secondary reduction of this maximum combustibility being affected by the after treatment at temperatures above this range. These variations of combustibility have their counterpart in the macroscopic changes of dimensions of coke blocks prepared under comparable conditions (7). From Table 32, for example, by increasing the maximum temperature of coking, the diameter and length of similarly carbonised charges of coal C are shown to decrease. The slower the rate of carbonisation the greater the contraction in length of comparable cokes, although differences in diameter are not so evident. These dimensional changes are due to volatile emission and/or graphitisation, and the tendency to reach some constant minimum value of both dimensions is apparent. This trend is corroborated by the results of the same Table, which show the alterations in size affected by increasing times of coking. Graphitisation, which is the principal factor, appears to be complete after six hours of

TABLE 31.

Analyses of a series of cokes prepared from the portions of coal B resting on defined screens.

Rate of heating to maximum temperature - 5°C/minute.
Rime of soaking at maximum temperature - 1 hour.

COAL B.

Mesh limits of Sample B.S.S.	Over 10	10 to 18	18 to 36	36 to 72	72 to 150
Moisture.	2.6	2.8	3.1	2.6	3.5
Volatile Matter less moisture.	2.6	2.4	2.6	2.3	3.0
Fixed Carbon.	92.5	91.4	86.8	85.9	80.3
Ash.	2.3	3.4	7.5	9.2	13.2
Volatile Matter, dry ash free.	2.7	2.6	2.9	2.6	3.6
Combustibility at 850°C.	3.783	3.300	3.055	3.065	3.294

TABLE 32.

Approximate dimensional changes on coking similarly packed coal charges under various conditions.

Coking Temp. °C.		500.	600.	700.	800.	900.	1000.	1100.	1200.
Heating Rate:									
5°C/minute	Diam.	3.0	3.0	2.9	2.8	2.8	2.7	2.8	2.7
	Length	11.8	11.8	11.2	10.9	10.9	10.8	10.8	10.7
3°C/minute	Diam.	3.0	2.9	2.8	2.8	2.7	2.7	2.8	2.7
	Length	11.8	11.4	11.0	10.8	10.8	10.7	10.8	10.8
Coking Time at above temp.		1 hour.							

Coking Time at 900°C.hrs.		0	¾	1⅓	3	6	12
	Diam.	2.9	2.8	2.9	2.8	2.8	2.8
	Length	11.0	11.0	10.9	10.9	10.9	10.9
Heating Rate.		5°C. per minute.					
Coking Temp.		900°C.					

Maximum Particle Size. B.S.S.		5	10	18	36	72	150
	Diam.	3.0	2.9	2.8	2.8	2.7	2.8
	Length	14.2	13.0	12.4	12.0	11.1	11.1
Heating Rate.		5°C. per minute.					
Coking Temp.		900°C.					

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heating at 900°C, although the more sensitive measurement of combustibility detected continued internal activity after a further six hours soaking. The greatest differences, however, are to be found in the relative dimensions of the coke blocks prepared from coal of various mean particle sizes, as shown in Table 32, and these differences are responsible for the comparable variations of combustibility, previously discussed. The dimensions of these coke blocks are a measure of a quality which has been alternatively named density equivalent or apparent density, a quality compounded of the true density of the coke material and porosity.

Combustibility thus becomes a function of only three fundamental characteristics -

(a). density equivalent, i.e., the weight of the standard sample of these experiments,

(b). degree of graphitisation, and

(c). ash content,

although each of these features (excepting the latter) is a further function of the coal charge from a chemical and physical aspect, the rate of carbonisation and the time and temperature of coking. The qualitative effect of these variables of carbonisation on the fundamental features of coke which determine its combustible value, have already been discussed but the expression of these effects in a single mathematical formula is as yet unsuccessful. Note too that the factors, (a), (b) and (c) assess the relative combustibilities of the solid fuels only. The contribution of the air supply in determining the absolute rate of combustion has already been considered in Chapter 2.

Concurrently with the experimental work on the combustible properties of the variety of cokes procurable from any one coking coal, some of the problems of carbonisation, as such, were investigated. While the amount and nature of the volatile matter of the plastic range determine the ability of a coal to cake, the physical appearance of a coke depends upon the rate of exhaustion or removal of the gases from the plastic mass.

When heated in a steel or Pythagoras crucible, a normal charge of coal C (72 mesh B.S.S.) was expelled by the accumulated pressure of the heavy emission of gas. Replacement of both these materials by a container of alundum, which is permeable to gases, reduced this exceedingly vigorous carbonisation to allow of controlled preparation of the series of cokes of Tables 26 to 30. By exhaustion of the gases of carbonisation under the partial vacuum created by a water pump, controlled coking was achieved in steel or Pythagoras crucibles. Two conditions attached to this practice. For successful carbonisation, it was only necessary to apply the vacuum in the temperature range of plasticity, and the greater the degree of vacuum at this stage of coke formation, the greater was the visual apparent density of the resultant coke. It is probable that the viscosity of the plastic fluid of coal liquefaction is also a factor determining the rate of dissipation of the internally developed pressure of the gases of carbonisation.

Carbonaceous blocks, which in all other respects were indistinguishable from each other, differed superficially with the type of container in which they were prepared. Using alundum, the surface of such blocks was covered with a powdery, non-adherent layer of about 1 mm. in depth on a 26 mm. diameter section. With the impermeable crucibles, steel and Pythagoras, however, the slight irregularities of the inside of these "moulds" were reproduced clearly on the hard resistant surface of the coke specimens. These differences are related to the restricted passage of the volatile matter to the body of the plastic mass in impermeable containers compared with the further alternative outlet offered by the alundum walls.

The gaseous evolution through semi-solid coal resembles in many respects the gaseous evolution of a rimming steel on solidification. In a longitudinal section of a coke from coal C there was to be seen the blown appearance of the top of the coke "ingot", the dense rim and bottom of instantaneous freezing and the gradual further solidification at inclinations of about

30° to the wall of the container as shown by the direction of the major axis of the ovoid vesicles of the coke. A transverse section revealed the increasing pore size from surface to centre.

The oxygen content of a coal, internal as well as that adsorbed on the surfaces, appears to be particularly detrimental to caking (40). The efficient inhibiting blanket which adsorption of oxygen (or nitrogen) may be is illustrated by the following experiment. A normally high caking index coal (18) was ground to 150 mesh B.S.S. and left in the open air for two months. After carbonisation the charge fell away to its original powdery state with no signs of the expected caking. The loss of this quality is a function of the time of exposure, however, and the particle size of the charge. The deterioration is most rapid in the first few weeks and especially with the finer coal charges.

Finally, four coals of caking index less than 7 were ground to -250 mesh B.S.S. and coked in a steel pot at 5°C/minute to 900°C. Slight coherence was shown but even this disappeared (with one exception) if the carbonisation was carried out in an alundum container or if the charge was coarser than the above screen limit, e.g., 36 mesh B.S.S. In the absence of any standard of comparison or reliable strength test, these results do not allow of any satisfactory conclusion being drawn, but they indicate possible methods of improving the caking quality of coals, at least on a laboratory scale.

CONCLUSION.

The function of coke in the blast furnace cannot be divorced from the other many chemical and physical reactions of the furnace and, in that respect, the research of this thesis, confined as it is to combustibility, can only define the activity of coke in the blast furnace from that aspect.

All ores have not the same ease of reduction. At any temperature, the extent of the reduction depends upon the CO/CO_2 ratio, the more easily reducible ores requiring the lesser ratio of these gases. The consumption of CO is also greater the higher the temperature of reduction. The rate of a gaseous reaction is many times greater than that which takes place between solids, and it is assumed that the bulk of the reduction in the shaft of the furnace is a result of gas attack. The amount of CO available for reducing the ore depends upon the rate of combustion of the coke, and this rate is a function of the rate and pressure of air supply, moisture, temperature and the coke itself. The sum of these will determine the suitability, or otherwise, of a particular coke, under specified conditions of air supply, to reduce satisfactorily a particular ore.

The production of the CO for the reduction of the ore is not the only property demanded of the coke. This CO must be formed at such a rate at the tuyere zone, that the temperature of the furnace at this level, and for some distance above, is sufficiently high to melt the reduced iron sponge and gangue coming from the shaft.

It would thus appear that the type of coke charge to the furnace should have the following properties:-

(a) that it remains unreactive, or exhibits a minimum of reactivity, towards CO_2 on travelling down the shaft;

(b) that at the tuyere zone, it should have a rate of combustion high enough to melt the products entering this zone from the shaft, and

(c) at this level, too, the amount of CO produced must be sufficient to perform the chemical reactions involved in the reduction of the ore in the shaft.

The type of log. $k/\frac{1}{T}$ and its position in the scale of log. k, which will satisfy the operating conditions of any one furnace, is the basis of development of the function of coke in the blast furnace. In the future it is hoped to correlate these curves with the operating results obtained on using these cokes, whose combustibility curves are known. A knowledge of the type of curve, producing the desired results most efficiently, and the conditions of coke manufacture, which determine this curve form, would at least enable the blast furnace manager to charge one less unknown quantity into his furnace. Whether some compromise will have to be made with the financial conditions involved in the production of such scientific cokes is outwith the province of this thesis.

The translation of the proven relationships of carbonisation conditions and combustibility to industrial practice must, of necessity, proceed slowly. Local peculiarities of the coal seams, oven design, consumer's requirements and by-product control are some of the factors to be considered before introducing new coking methods. Nevertheless, in broad principle, the main conditions controlling coke manufacture (and their effect on combustibility) have been detailed here, and these, in their very simplicity, offer ways to the goal of controlled reproduction of coke qualities - qualities which will assure the suitability and efficient performance of a coke under the specified conditions of its proposed use.

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